CORROSION OF METALS EXPOSED TO COMBUSTION PRODUCTS
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ATLANTA SCHOOL OF AEROSPACE ENGINEERING..

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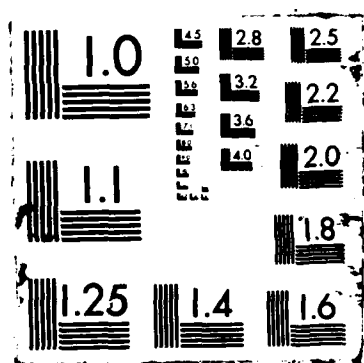
REPORT DOCUMENTATION PAGE

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1a. REPORT SECURITY CLASSIFICATION: Unclassified		1b. RESTRICTIVE MARKINGS		
2a. SECURITY CLASSIFICATION AUTHORITY		3. DISTRIBUTION/AVAILABILITY OF REPORT Approved for public release; distribution unlimited		
2b. DECLASSIFICATION/DOWNGRADING SCHEDULE				
4. PERFORMING ORGANIZATION REPORT NUMBER(S)		5. MONITORING ORGANIZATION REPORT NUMBER(S)		
6a. NAME OF PERFORMING ORGANIZATION Georgia Institute of Technology School of Aerospace Engineering	6b. OFFICE SYMBOL (If applicable)	7a. NAME OF MONITORING ORGANIZATION Naval Research Laboratory		
6c. ADDRESS (City, State and ZIP Code) Atlanta, Georgia 30332.		7b. ADDRESS (City, State and ZIP Code) Washington, DC 20375		
8a. NAME OF FUNDING/SPONSORING ORGANIZATION	8b. OFFICE SYMBOL (If applicable)	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER		

8c. ADDRESS (City, State and ZIP Code)	10. SOURCE OF FUNDING NOS.			
	PROGRAM ELEMENT NO.	PROJECT NO.	TASK NO.	WORK UNIT NO.

11. TITLE (Include Security Classification) Corrosion of Metals Exposed to Combustion Products Generated During Shipboard Fires

12. PERSONAL AUTHOR(S) E. A. Powell, B. T. Zinn

13a. TYPE OF REPORT Final	13b. TIME COVERED FROM _____ TO _____	14. DATE OF REPORT (Yr., Mo., Day)	15. PAGE COUNT 77

16. SUPPLEMENTARY NOTATION Contract monitored by Frederick W. Williams, Code 6180, Naval Research Laboratory

17. COSATI CODES			18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)
FIELD	GROUP	SUB. GR.	Corrosion Fire Hazards
			Combustion Products Polymeric Materials
			Smoke

19. ABSTRACT (Continue on reverse if necessary and identify by block number)

A study was conducted to assess the post-fire corrosion hazard of the materials used in power and communications cables aboard ships to a number of metals used in shipboard structures and systems. Small metal specimens were exposed to the combustion products generated in full scale cable fire tests conducted at the U. S. Coast Guard Fire and Safety Test Detachment facility in Mobile, Alabama. Metal coupons were installed in the fire test compartment aboard an instrumented ship for three tests. In the first test (W-11), the fuel or source material was a mixture of two proposed new cables, MIL-C-24640 and MIL-C-24643. The other two tests involved a currently used cable, MIL-C-915E, Amendment 2. In the first of the MIL-C-915E tests (W-13), the cables failed to ignite and the metal specimens were exposed to the combustion products of smoldering or nonflaming combustion. In the second of the MIL-C-915E tests (W-13A), the cables ignited and the metals were exposed

20. DISTRIBUTION/AVAILABILITY OF ABSTRACT UNCLASSIFIED/UNLIMITED ☒ SAME AS RPT. ☐ DTIC USERS ☐	21. ABSTRACT SECURITY CLASSIFICATION Unclassified	
22a. NAME OF RESPONSIBLE INDIVIDUAL	22b. TELEPHONE NUMBER (Include Area Code)	22c. OFFICE SYMBOL

DD FORM 1473, 83 APR EDITION OF 1 JAN 73 IS OBSOLETE.

Unclassified
SECURITY CLASSIFICATION OF THIS PAGE

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to the heavy sooty smoke produced during flaming combustion. The metallic specimens or target materials were HY80 steel, type 304 stainless steel, brass, and Monel 400. The metallic coupons were stored under both moderate and high humidity conditions after the fire tests. During this post-fire period, which lasted nearly a year, the specimens were weighed and observed periodically to assess the degree of corrosion.

The HY80 steel experienced the greatest amount of corrosion as assessed by mass increase, mass of corrosion products removed by cleaning, and macroscopic appearance. The greatest corrosion mass increases occurred with the MIL-C-915E cable as the source material and post-fire storage at high humidity. Mass increases for these specimens were about 10-12 mg/cm^2 during the high humidity period (20-190 days), which was about 44 times greater than the mass increases of the controls which were also exposed to high humidity. These mass increases were also about 12 times larger than the corresponding mass increases for the specimens which remained at 70% humidity. For this test, vertical location had little effect on corrosion rates in spite of smoke stratification effects. For the MIL-C-24640/24643 source material, the corrosion mass increases were much smaller, being significant only for the specimens stored under high humidity. Here the mass increases were five to six times greater than those for the control specimens. For both source materials the corrosion products consisted of hydrated ferric oxide or rust, and the mass increases measured represent the mass of oxygen and water which combined with the iron in the steel.

The brass specimens exposed to the MIL-C-915E combustion products at the upper location also experienced significant corrosion. Most of the mass increase occurred during the fire test and immediately thereafter. The corrosion products were hydrated copper and zinc salts, probably chlorides, which formed encrustations of blue-green and white crystals on the surfaces of the specimens. Most of the mass increase of the brass specimens was probably due to water attracted by these hygroscopic salts. The brass specimens from the lower rack did not exhibit any crystalline material, but were covered with a very dark tarnish. The mass increases of these specimens were only a tenth as great as those from the upper station. The brass specimens from the MIL-C-24640/24643 test showed varying degrees of discoloration due to tarnish and interference tints, which indicate the formation of thin oxide or sulfide films. These films tend to inhibit further corrosion. The mass increases for these specimens were very small, and the damage to the material was insignificant.

The type 304 stainless steel and Monel 400 materials were found to be fairly resistant to corrosion from the combustion products of both source materials. Although small patches of pale green crystalline material appeared on some of the Monel 400 specimens from the MIL-C-915E test, the amount of corrosion for these specimens was very small and did not cause any significant damage to the material.

The results of this study show that the older type cables present a severe corrosion hazard to some commonly used metals when exposed to their corrosion products in a fire. The corrosion problem is most serious when the metals are in a high humidity environment after the fire. This study also showed that by using new cable materials which produce less smoke and corrosive gas, the corrosion hazard can be greatly reduced.

CORROSION OF METALS EXPOSED TO COMBUSTION PRODUCTS

GENERATED DURING SHIPBOARD FIRES

E. A. Powell and B. T. Zinn

Georgia Institute of Technology

School of Aerospace Engineering

Atlanta, GA 30332

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CONTENTS

Abstract

A study was conducted to assess the post-fire corrosion hazard of the materials used in power and communications cables aboard ships to a number of metals used in shipboard structures and systems. Small metal specimens were exposed to the combustion products generated in full scale cable fire tests conducted at the U. S. Coast Guard Fire and Safety Test Detachment facility in Mobile, Alabama. Metal coupons were installed in the fire test compartment aboard an instrumented ship for three tests. In the first test (W-11), the fuel or source material was a mixture of two proposed new cables, MIL-C-24640 and MIL-C-24643. The other two tests involved a currently used cable, MIL-C-915E, Amendment 2. In the first of the MIL-C-915E tests (W-13), the cables failed to ignite and the metal specimens were exposed to the combustion products of smoldering or nonflaming combustion. In the second of the MIL-C-915E tests (W-13A), the cables ignited and the metals were exposed to the heavy sooty smoke produced during flaming combustion. The metallic specimens or target materials were HY80 steel, type 304 stainless steel, brass, and Monel 400. The metallic coupons were stored under both moderate and high humidity conditions after the fire tests. During this post-fire period, which lasted nearly a year, the specimens were weighed and observed periodically to assess the degree of corrosion.

The HY80 steel experienced the greatest amount of corrosion as assessed by mass increase, mass of corrosion products removed by cleaning, and macroscopic appearance. The greatest corrosion mass increases occurred with the MIL-C-915E cable as the source material and post-fire storage at high humidity. Mass increases for these specimens were about 10-12 mg/cm^2 during

the high humidity period (20-190 days), which was about 44 times greater than the mass increases of the controls which were also exposed to high humidity. These mass increases were also about 12 times larger than the corresponding mass increases for the specimens which remained at 70% humidity. For this test, vertical location had little effect on corrosion rates in spite of smoke stratification effects. For the MIL-C-24640/24643 source material, the corrosion mass increases were much smaller, being significant only for the specimens stored under high humidity. Here the mass increases were five to six times greater than those for the control specimens. For both source materials the corrosion products consisted of hydrated ferric oxide or rust, and the mass increases measured represent the mass of oxygen and water which combined with the iron in the steel.

The brass specimens exposed to the MIL-C-915E combustion products at the upper location also experienced significant corrosion. Most of the mass increase occurred during the fire test and immediately thereafter. The corrosion products were hydrated copper and zinc salts, probably chlorides, which formed encrustations of blue-green and white crystals on the surfaces of the specimens. Most of the mass increase of the brass specimens was probably due to water attracted by these hygroscopic salts. The brass specimens from the lower rack did not exhibit any crystalline material, but were covered with a very dark tarnish. The mass increases of these specimens were only a tenth as great as those from the upper station. The brass specimens from the MIL-C-24640/24643 test showed varying degrees of discoloration due to tarnish and interference tints, which indicate the formation of thin oxide or sulfide films. These films tend to inhibit further corrosion. The mass increases for these specimens were very small, and the damage to the material was insignificant.

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The results of this study show that the older type cables present a severe corrosion hazard to some commonly used metals when exposed to their corrosion products in a fire. The corrosion problem is most serious when the metals are in a high humidity environment after the fire. This study also showed that by using new cable materials which produce less smoke and corrosive gas, the corrosion hazard can be greatly reduced.

INTRODUCTION

This report describes the efforts conducted for the Naval Research Laboratory under Contract No. SFRC N00014-85-K-2012 entitled "Corrosion of Metals Exposed to Combustion Products Generated During Shipboard Fires." This work, which was performed during the period 27 March 1985 to 26 March 1986, is concerned with the corrosion of small metallic specimens which were exposed to the combustion products generated in full scale cable fire tests conducted at U.S. Coast Guard, Fire and Safety Test Detachment, Mobile, Alabama. Metal samples were installed in the fire test compartment aboard an instrumented ship for three of these tests: W-11 on 15 May 1985, W-13 on 26 June 1985, and W-13A on 27 June 1985. In Test W-11 the fuel or source material was a proposed new cable, MIL-C-24640 and 24643, while in Tests W-13 and W-13A the source material was the older cable, MIL-C-915E, Amend. 2. The new cables were found to be much more resistant to fire and produced much less smoke and corrosive gas. The metallic specimens or target materials were HY80 steel, type 304 stainless steel, brass, and Monel 400. In these tests the metallic specimens were exposed to the fire environment and then observed over a period of nearly a year to assess the degree of corrosion.

This research project is an extension of earlier work sponsored by the Naval Research Laboratory (SFRC N00014-82-K-2066) in which similar metallic specimens were exposed to the combustion products generated in the large-scale pressurizable fire test facility (FIRE I) at the Naval Research Laboratory. In this earlier test, which was conducted on 21 June 1983, the source material was PVC nitrile rubber coated with Ocean 634 primer and Ocean 9788 intumescent

paint. HY80 steel and cold rolled steel specimens became heavily corroded in the 20 days following the fire, and the rusting process was vastly accelerated by high humidity. Details of the test procedures and a discussion of the results are given in Reference 1.

This program has been directed by principal investigators Dr. Ben T. Zinn and Dr. Eugene A. Powell in the School of Aerospace Engineering of the Georgia Institute of Technology. Dr. Zinn was responsible for the administrative and managerial aspects of this research program, while Dr. Powell was responsible for the planning, design and conduct of the corrosion experiments and the corrosion assessment methods.

EXPERIMENTAL CONFIGURATION AND PROCEDURES

Fire Compartment and Cable Configuration

The test area of the ship is shown schematically in Figure 1. It consisted of the room of fire origin, a forward and after compartment, and a passageway. The 80 plus cables were installed in a three tier cable bundle suspended from the overhead, according to Navy specifications. The cables penetrated the forward and after bulkheads through collars which were packed with plastic sealer material (MIL-I-3064B, Type HF). Some cables originated from a mock motor generator, traversed toward the forward bulkhead, looped upwards to join the cable bundles, and then ran forward and aft in the compartment. The cable loop projected over the aft edge of the fuel pan. The corrosion test specimens were mounted in the fire compartment as shown in Figure 1.

Test Specimens and Mounting Configuration

Small test specimens or coupons of HY80 steel, type 304 stainless steel, brass, and Monel 400 (64% Ni, 32% Cu) were fabricated from stock provided by the Navy (HY80 steel) or obtained commercially. For the HY80 steel the specimens were cut from 6.35 mm (1/4 in) thick plate in strips 6.35 mm (1/4 in) wide and 101.6 mm (4 in) long. The ends of the HY80 steel specimens were machined down to a thickness of about 1 mm to form mounting tabs about 6 mm long. The stainless steel and brass coupons were cut from 0.79 mm (1/32 in) sheet stock into flat strips 19.1 mm (3/4 in) wide and 101.6 mm (4 in) long.
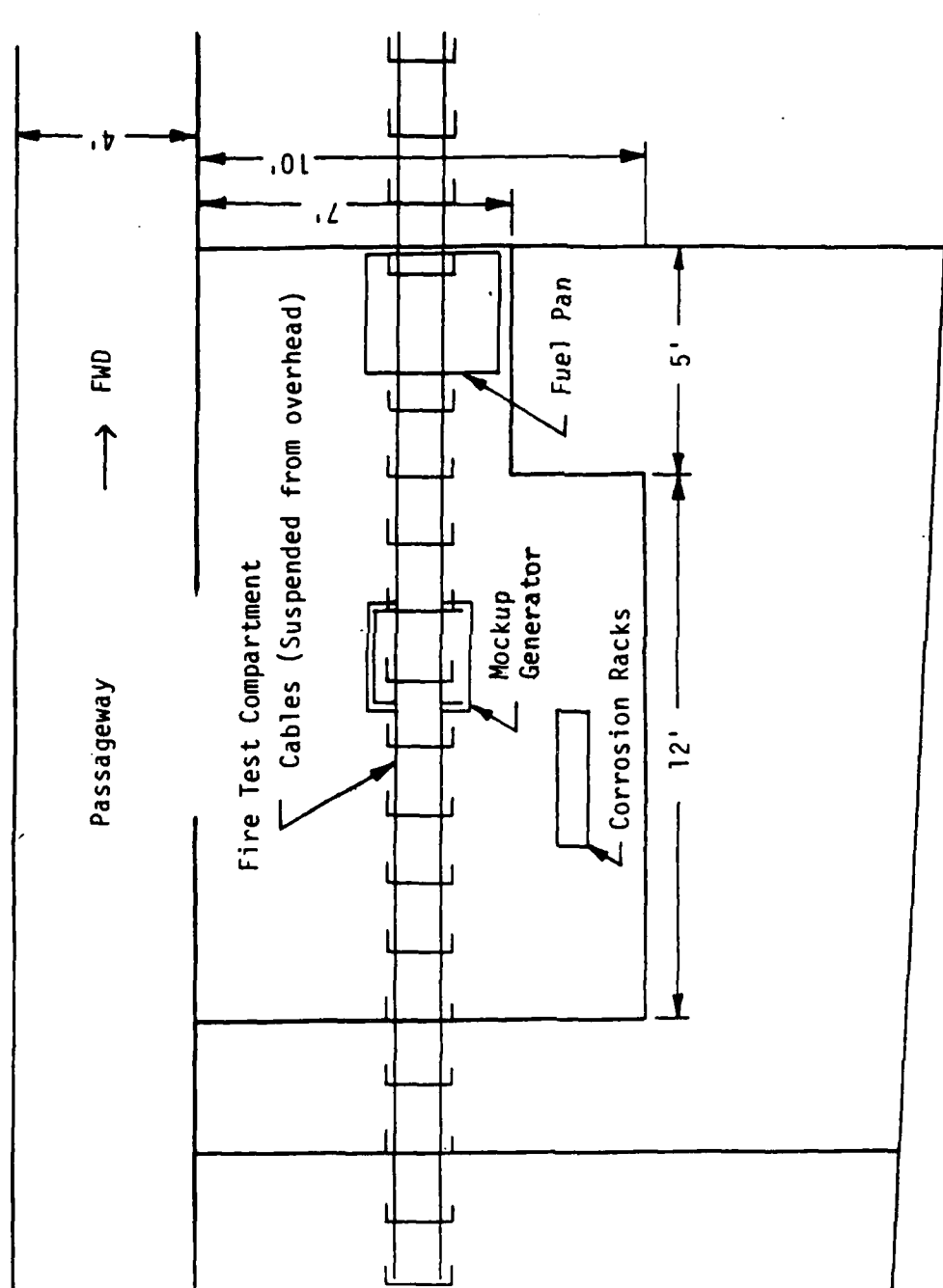
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Figure 1. Fire Test Configuration.

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The Monel 400 specimens were prepared by cutting 6.35 mm (1/4 in) diameter tubing into 101.6 mm (4 in) long sections and flattening the ends to form mounting tabs. A 3 mm diameter hole was drilled near the ends of each of the specimens to facilitate mounting and handling. The test specimens are shown schematically in Figure 2. The average weight and surface area of the specimens of each material are given in Table 1.

Table 1. Weight and Surface Area of Coupons

Material	Average Weight (g)	Surface Area (cm^2)	Number of Specimens
HY80	30.02	25.6	44
304 SS	14.02	38.4	44
Brass	13.44	38.4	44
Monel 400	13.47	20.3	36

The test specimens were supported in racks as shown in Figure 3. These racks were 76.2 cm (30 in) long and 10.16 cm (4 in) wide, and they allowed 48 specimens to be mounted in two parallel rows of 24 specimens each. The average separation of adjacent specimens was about 3.2 cm (1 1/4 in). The specimens were suspended from the top rails using steel S-hooks and the lower ends of the specimens were secured to the bottom rail using fine brass wire.
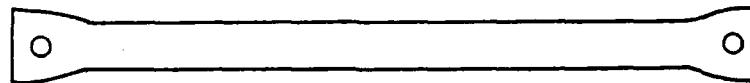
Two racks of test specimens at different heights above the deck were mounted in the fire compartment in the horizontal location shown in Figure 1. The upper rack, which is hereafter referred to as Station 1, was located 170 cm (67 in) above the deck, measured from the center of the test specimens.

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HY80 Steel
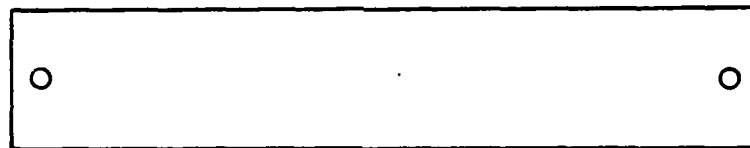
Stainless Steel and Brass

Monel 400

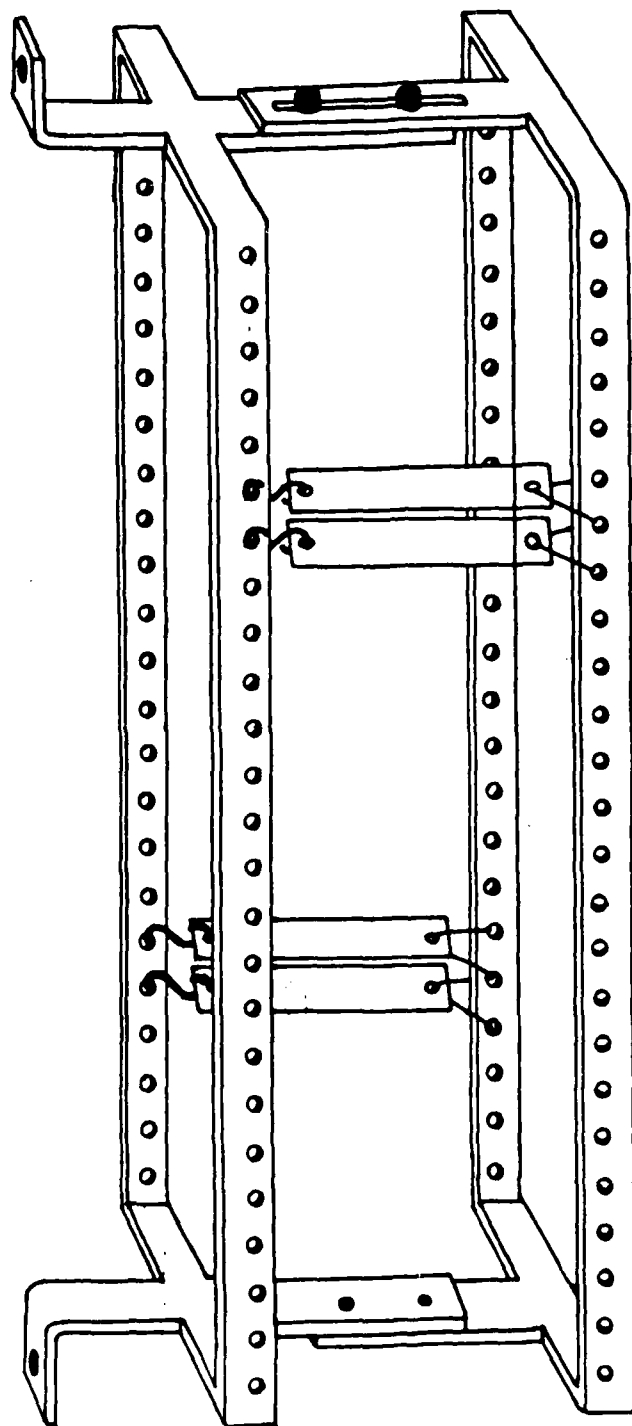Figure 2. Corrosion Test Coupons.

Figure 3. Test Specimen Rack.

The lower rack (Station 2) was located 79 cm (31 in) above the deck. Both racks were located 61 cm (24 in) out from the bulkhead. These locations were based on the results of earlier tests in the series which showed much more smoke at the higher levels in the fire compartment. A photograph of the test racks and specimens installed in the fire compartment just prior to a test is shown in Figure 4.

Preparation of Coupons for Fire Tests

Cleaning of Coupons. All of the metal coupons were cleaned prior to the fire tests. A commercial abrasive metal cleaner was used to remove tarnish from the brass specimens and rust from the HY80 steel specimens. An identification number was then engraved at one end of each coupon. Finally all of the coupons were cleaned with methanol and acetone and then sealed in Plexiglas transport/storage cases to await testing.

Selection and Weighing of Coupons. A number of replicate coupons of each material were selected for each of the two planned fire tests. These were further subdivided into two groups according to the vertical location in the fire compartment. The numbers of replicate specimens for each group and test are given in Table 2. Fewer specimens of Monel 400 were used due to the limited amount of this material available prior to the fire tests. Fewer specimens were also used in Test W-13 due to the limited availability of HY80 steel, stainless steel, and brass in the same batches as used in the earlier test conducted at the Naval Research Laboratory in June 1983.

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Photo to be supplied by N.R.L.

Figure 4. Test racks with metal coupons in
fire compartment before a test.

Table 2. Distribution of Replicate Specimens.

Test	Station	HY80	SS 304	Brass	Monel 400
W-11	1	12	12	12.	9
	2	12	12	12	9
W-13	1	9	9	9	8
	2	9	9	9	8

. The coupons for Test W-11 were weighed at Georgia Tech 12 days prior to the test, while the coupons for Test W-13 were weighed one day before the test. Since the coupons were stored in a clean dry environment between weighing and testing, corrosion occurring during this time was insignificant. All weighings were performed using a Mettler Model AE 163 semi-micro balance. This is a dual range electronic balance with readability to 0.01 mg for weights less than 30 g and readability to 0.1 mg for weights between 30 g and 160 g.

Installation in Mounting Racks. The coupons for both vertical stations were installed in their mounting racks a few hours before the fire tests. Due to the complexity of the flow patterns and smoke movement in the fire compartment, it was likely that the deposition of smoke particulates on the metal coupons would be sensitive to location on the mounting rack. Therefore coupons of the same material were not all grouped together on the mounting racks. Instead, the coupons for Test W-11 were divided into 12 groups as shown in Figure 5, with each group containing one coupon of each material (except Monel 400 for a few groups). This arrangement was expected to reduce the possibility of experimental bias due to location on the rack. The coupons
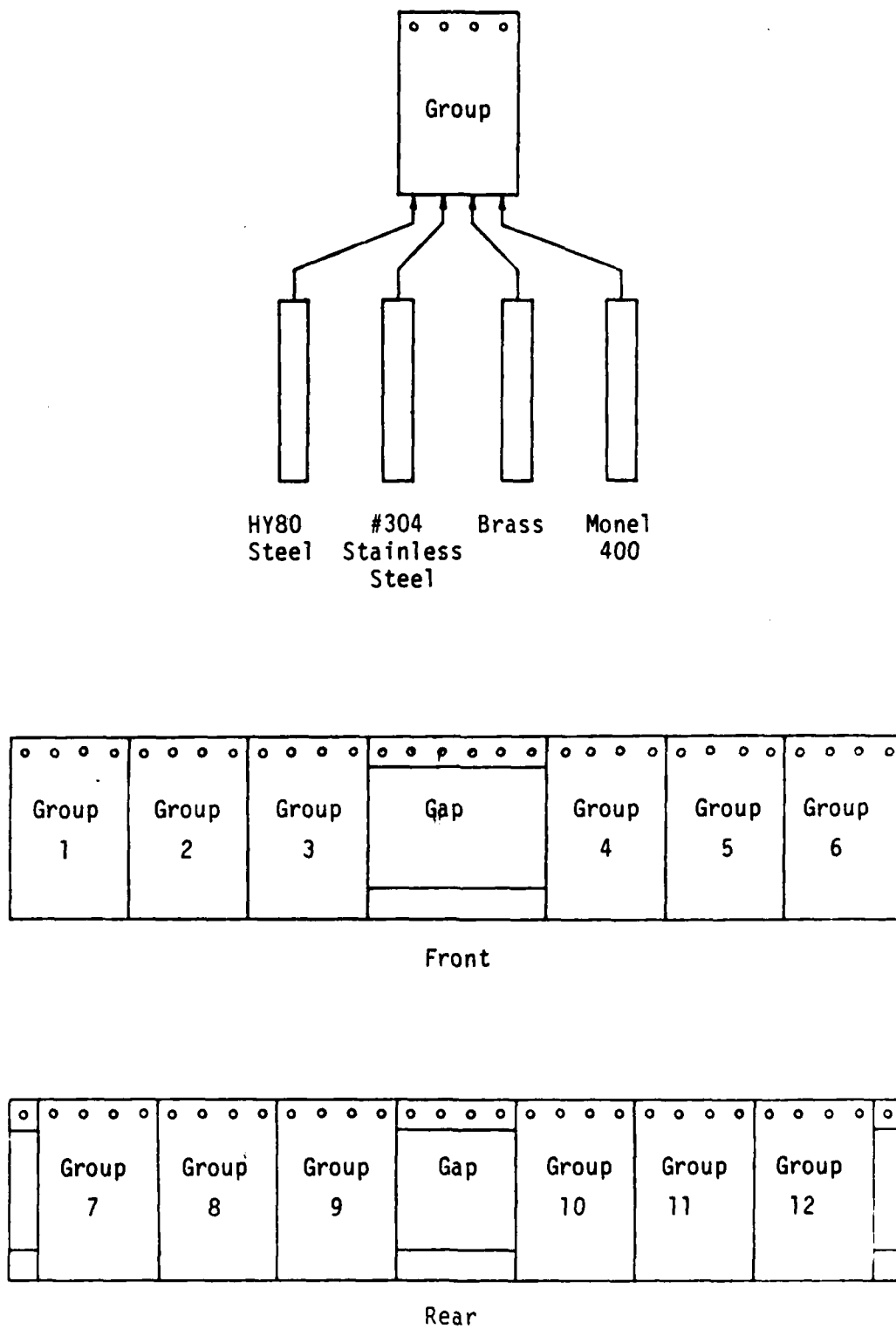
Group

HY80   #304   Brass   Monel
Steel   Stainless   400
         Steel

Group 1 | Group 2 | Group 3 | Gap | Group 4 | Group 5 | Group 6

Front

Group 7 | Group 8 | Group 9 | Gap | Group 10 | Group 11 | Group 12

Rear

Figure 5.   Specimen Mounting Configuration for Test W-11.

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for Test W-13 were arranged in a similar pattern to those of Test W-11, but with 5 groups in front (toward the cables) and 4 groups in back.

Post-Fire Procedures

About one hour after the fire tests were completed the specimen racks were taken out of the fire compartment. The metal coupons were then removed from the mounting racks and transferred to a Plexiglas storage and transport case (Figures 6 and 7).

Two storage cases were constructed, one for each test. Each case was a box 44 cm (17 1/4 in) wide, 52 cm (20 1/2 in) long, and 6.7 cm (2 5/8 in) deep fitted with a removable tray. The tray was partitioned lengthwise into four sections for storing the metal coupons. The partitions were provided with vertical slots for holding the coupons at the ends. The tray could hold up to 150 metal coupons, each separated from its neighbors by a 1.25 cm (1/2 in) gap. This arrangement protected the coupons with their adherent combustion products and corrosion products from contact with each other and from contamination from the environment.

The trays occupied the upper half of the storage boxes, while the lower half could be used for the storage of water soaked sponges to provide a high humidity environment for the coupons if desired. The bottom of the specimen tray was perforated with numerous 6.35 mm (1/4 in) diameter holes to allow the water saturated air in the lower compartment to reach the corrosion test specimens. However, direct contact of the test specimens with liquid water was prevented by this configuration. The test specimens were sealed from the

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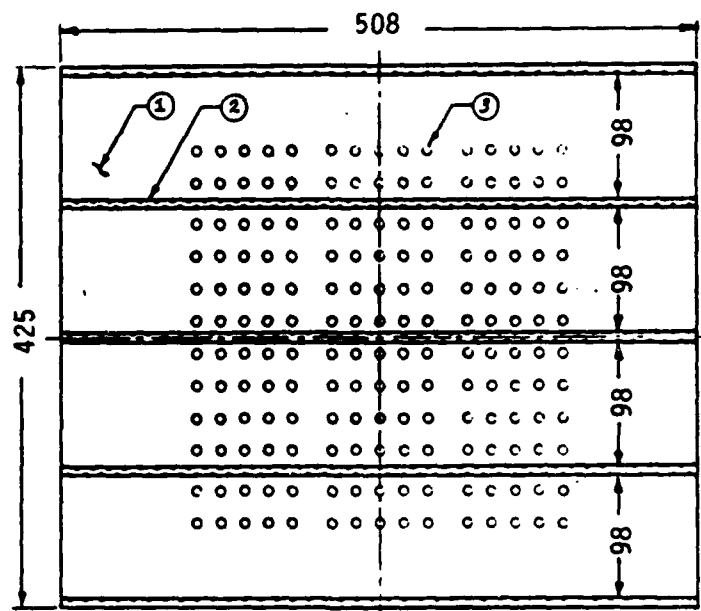
Removable Specimen Tray
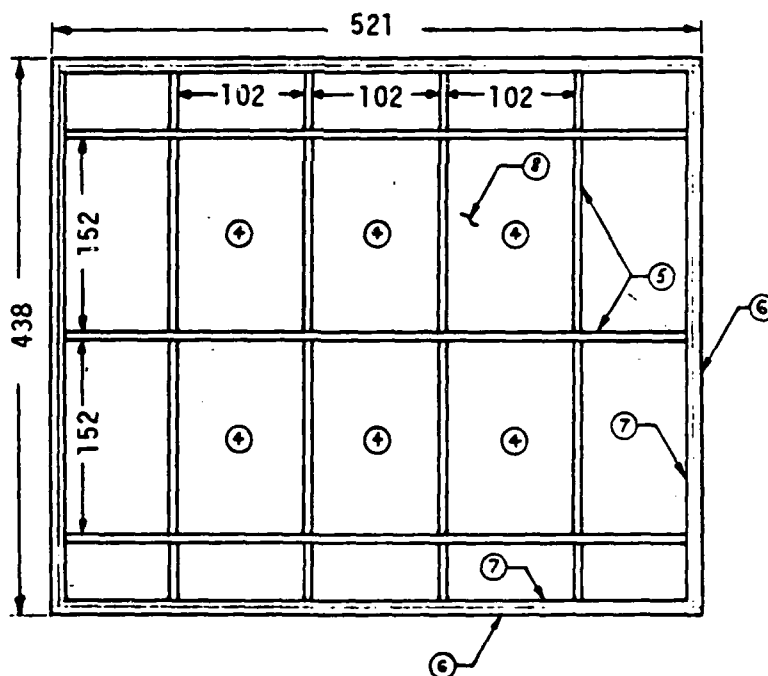
1. Perforated floor of tray
2. Slotted partitions, 25 mm high
3. 6.4 mm dia. holes
4. Sponge compartments

5. Inner partitions, 25 mm high
6. Outer side walls, 67 mm high
7. Inner side walls, 25 mm high
8. Floor of case

Figure 6. Schematic of Storage and Transport Case
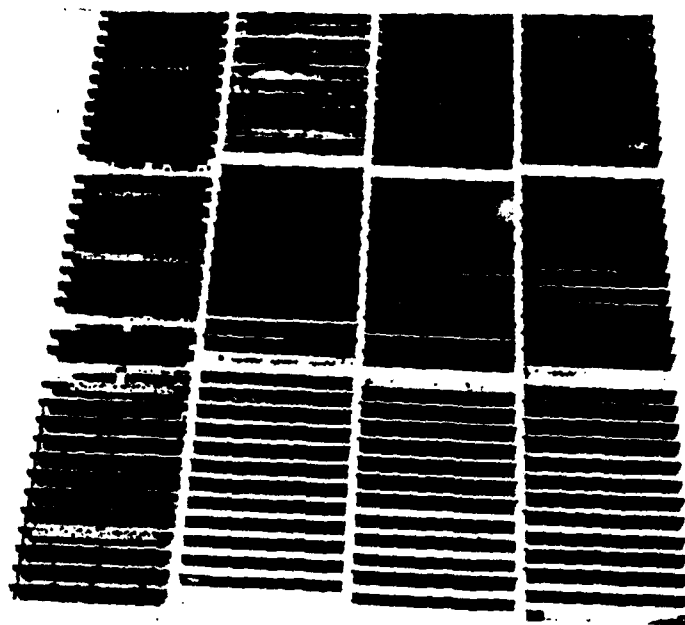with Removable Specimen Tray.

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Figure 7. Storage and transport case with coupons in place, lid removed.

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external environment by a tight-fitting Plexiglas lid which allowed viewing of the specimens at all times.

The sealed storage cases (without sponges) were then transported back to the Coast Guard Base for weighing of the coupons. All of these weighings were done with the Mettler AE 163 balance, which was brought to Mobile from Georgia Tech. The weighings were begun about two hours after the coupons were removed from the fire test compartment and were completed about two hours later. The specimen cases were then resealed, stored in the automobile overnight, and then transported back to Georgia Tech the next day.

All of the coupons were stored in the Plexiglas cases for a period of time under moderate humidity conditions (i.e., without the water-soaked sponges). This period, which included transportation to Georgia Tech, lasted 15 days for the Test W-11 coupons and 20 days for the Test W-13 coupons. During most of this time the specimens were in an air conditioned laboratory at a temperature of about 22°C and a relative humidity of about 72%. During the moderate humidity phase, the W-11 and W-13 coupons were weighed at approximately weekly intervals.

Immediately after the last weighing during the moderate humidity phase for each test the high humidity phase was begun. The high humidity phase for Test W-11 was initiated before Test W-13 was conducted. The water soaked sponges were placed in the lower compartments of one of the Plexiglas storage cases and half of the metal coupons from Test W-11 were transferred to it. The remaining W-11 specimens were stored under moderate humidity along with the W-13 specimens in the other Plexiglas case which later was taken to Mobile

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for Test W-13. At the end of the moderate humidity phase for Test W-13, half of these specimens were transferred to the high humidity storage case. For the remainder of the post-fire corrosion assessment period, two groups of coupons were monitored for each test: a moderate humidity group and a high humidity group. Of course each humidity group was equally represented by specimens from Station 1 and Station 2.

The specimens from both humidity groups for each test were weighed at regular intervals for the remainder of the post-fire period. The entire post-fire period lasted 237 days for the W-11 specimens and 190 days for the W-13 specimens, except that it was extended about 100 days for the HY80 steel coupons from both tests. *f*ter this last weighing, the sponges were removed from the high humidity storage case and the post-fire observation period was terminated.

Control Specimens

In order to properly assess the corrosive effect of the combustion products on the metal coupons, control specimens were used which were not exposed to the fire environment but were stored under identical post-fire conditions. For each fire test, one coupon of each material remained in the Plexiglas case during the fire test and the moderate humidity phase of the post-fire period. These control specimens were later transferred to the high humidity environment along with the high humidity group of coupons. The control specimens were periodically weighed and examined along with the specimens which were exposed to the combustion products. The controls were

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then used as a basis for comparison to determine the corrosive effects of the combustion products.

CABLE FIRE TESTS

Test W-11

Test W-11 was conducted on 15 May 1985 using the proposed new low smoke, fire resistant cables (MIL-C-24643 and 24640). The fuel used to initiate the cable fire was 15.2 liters (4.0 gal) of ethyl alcohol in a 102 cm (3 ft) square fire pan. Previous tests without cables showed that the ethanol fuel itself contributed a negligible amount of smoke to the fire. The ethanol fuel was ignited at 14:00 CDT thus beginning the fire test. The ethanol burned for at least 16 minutes, but the cables were very slow to ignite. Flames were seen coming from the fuel pan for several minutes after the ethanol should have been exhausted. These were found to be melted material from the cables which was burning in the fire pan. Small flames were also seen on the vertical section of the cables near the fire pan, but these burned for only about half an hour. The fire did not propagate along the horizontal runs of the cables, and smoke levels were low throughout the test. The corrosion specimens were easily seen on the video monitor throughout the test. The metal specimens were removed from the fire test compartment at about 15:30 CDT.

The corrosion specimens were inspected immediately after the fire test. All of the coupons looked very clean with only a few deposited soot particles visible. The brass specimens from Station 1 (upper level), where the highest temperatures occurred, showed noticeable tarnish. The specimens were weighed in an air conditioned room in the F&STD building on the Coast Guard base between 17:30 and 19:30 CDT.

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Test W-13 and W-13A

These tests were originally planned as a single test, but the unexpected failure of the cables to ignite on the first attempt (W-13) led to a second attempt with the same cables (W-13A) the next day.

Test W-13 was conducted on 26 June 1985 using the older MIL-C-915E Amend 2 cables. Previous tests showed that this cable propagates flame readily, producing large quantities of smoke and corrosive gases. As in Test W-11 the ignition source was 15.2 liters of ethanol in a 102 cm square fire pan. The fuel was ignited at 12:18 CDT and the progress of the fire was observed on video monitors. Flames from the burning ethanol were observed to impinge on the vertical section of the cables which projected over the fire pan. Flames were visible for nearly 30 minutes rising from the fire pan, but the cables themselves never ignited. Since the ethanol is exhausted after only 18 or 19 minutes, the flames seen later were probably due to melted material from the cables burning in the fire pan. The test was terminated about ten minutes after these flames extinguished. Smoke levels seen on video during the test were very light, and at no time was the compartment obscured.

The corrosion specimens were left in the fire compartment overnight to await the second attempt (W-13A) with a larger fuel pan and a greater quantity of fuel. The corrosion specimens were removed from the fire compartment and inspected in the morning before the second test. The HY80 steel coupons were a light uniform red brown color, presumably due to rust, at both upper and lower stations (the lower seemed to have more rust). The brass specimens at the upper station were dull, while those from the lower station were still

bright. The stainless steel and Monel coupons appeared clean with little or no visible smoke deposition.

Two sets of coupons from each rack (one front and one rear) were removed before the second burn. Thus, for each material, one coupon from each vertical station and each humidity group was selected for post-fire assessment of corrosion due to the exposure to the smoke generated by smoldering or non-flaming combustion of the cable jacket material which occurred during Test W-13. These specimens were sealed in the Plexiglas case at 8:45 CDT, and the remaining coupons were reinstalled in the fire compartment about one hour later.

Test W-13A was conducted on 27 June 1985, using the same cables as in Test W-13 which were left undisturbed in the fire compartment during the interim. The ignition source was increased to 30.4 liters (8 gal) of ethanol in a 136 cm (4 ft) square fire pan. The fuel was ignited at 9:45 CDT and the first light smoke was seen about 9 minutes later. The cables finally ignited about 38 minutes after the start of the test with a large ball of fire, after which flames were seen on the upper bend of the cable loop from the mock generator. Two minutes later the fire compartment was heavily obscured by smoke, and the flames on the cables were best seen with the infrared (IR) camera. Flames were seen rising from the fire pan for about 50 minutes after fuel ignition, but during the last part of this period they were probably due to burning melted cable jacket material which had fallen into the fire pan. About one hour after the start of the test, falling droplets of melted and burning PVC jacket material were first seen on the IR image. By this time the IR camera showed a vigorous fire with much turbulence on the upper run of

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cables above the fire pan. About 20 minutes later the lower loop of cable above the fire pan was also seen burning on the first video camera (the IR camera was turned off due to excessive temperature). From topside, dense grey smoke was observed coming from the corridor exit. This smoke appeared to be a mixture of soot and tarry droplets.

After about 105 minutes a spectacular phenomenon was observed on the second video camera. Combustible gases collecting in the ceiling area above the horizontal run of cables would occasionally ignite, and waves of flame would spread across the ceiling with tongues of flame spreading downward and then extinguishing. This process repeated every minute or so.

At 113 minutes into the test, flames on the horizontal run of cables first entered the field of view of the second video camera. These flames slowly propagated toward the aft bulkhead. The flaming region was estimated to be about 50 cm (20 in) long, behind which the cable was completely charred and burned out. Flaming drops of melted cable jacket material were frequently seen falling from the leading edge of the flaming region. At 130 minutes, the flaming region reached the middle of the horizontal cable run, and these flames exhibited a striking cellular pattern on the underside. During this time occasional flare-ups of pockets of combustible gases continued to be observed. The cable fire continued burning vigorously until it reached the aft bulkhead at 160 minutes. Thereafter it gradually diminished until the last tiny flickering flames were seen at 13:40 CDT, nearly four hours after the test began.

The corrosion specimen racks were removed from the fire compartment at 14:25 CDT, and they were taken to the air conditioned control room where the coupons were transferred to the Plexiglas case. The coupons were weighed at the Coast Guard base three hours later.

The corrosion specimens were inspected while being weighed. The coupons of HY80 steel, #304 stainless steel, and Monel 400 from the upper station were covered with heavy deposits of sooty black and grey material with a fluffy texture. The brass specimens, however, appeared surprisingly different, with a very black, apparently wet, smooth deposit. The average weight gains of the brass specimens were also about 20 times larger than those of the other materials. It appears that a hygroscopic corrosion product was formed on the surface of the brass which attracted large quantities of water from the environment. The specimens from the lower rack exhibited little surface deposit, and with the exception of the HY80 steel the weight gains were smaller. The HY80 steel specimens exhibited a light coating of rust which accounts for the higher weight gain.

RESULTS OF TEST W-11

The metal specimens in Test W-11 were exposed to the combustion products generated by the proposed new cable, MIL-C-24640 and 24643. The initial mass increases for these specimens are given in Table 3, where both absolute mass increase and mass increases per unit area are tabulated. These mass increases for HY80 steel, #304 stainless steel and Monel 400 are probably due entirely to deposition of smoke particulates, but they are very small and near the limits of sensitivity of the analytical balance. This is consistent with the very low levels of smoke observed during Test W-11. The mass increases for the brass specimens, however, are significantly larger, and they probably are due to the formation of thin oxide films or tarnish during the fire exposure period. The tarnish was easily visible on the brass specimens from the upper station, where the average mass increase was four times larger than that for any other specimen group.

During the post-fire corrosion assessment period, which lasted 237 days (338 days for HY80 steel), the mass increase due to corrosion was determined by periodic weighings. At the end of this period macroscopic photographs were made of selected specimens which showed significant corrosion. Finally the specimens were cleaned to remove any corrosion products and weighed to determine the mass of metal lost due to corrosion. The results are discussed separately for each of the materials in the remainder of this section.

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Table 3. Initial Weight Gains for Test W-11

Material	Station	Average Weight Increase (mg)	Weight Increase per Unit Area (mg/cm^2)
HY80 Steel	1	$- 0.1 \pm .1$	$< .004$
	2	$0.0 \pm .1$	$< .004$
#304 Stainless Steel	1	$0.02 \pm .01$	$< .0005$
	2	$0.01 \pm .01$	$< .0003$
Brass	1	$0.43 \pm .01$	0.0111
	2	$0.10 \pm .01$	0.0026
Monel 400	1	$0.02 \pm .01$	$< .001$
	2	$0.09 \pm .01$	$.004$

HY80 Steel

Gravimetric data for the HY80 steel specimens are presented in Figure 8, where the mass increase per unit area (Δm/A) is plotted versus elapsed time. These curves illustrate the drastic effect of ambient humidity upon the corrosion process. For the first 15 days after the fire test, while all specimens were at about 70% humidity, the mass increase was negligible. After the humidity was increased to nearly 100%, the specimens in the high humidity group increased steadily in mass, reaching Δm/A of about 0.7 mg/cm^2 after about 320 days. The specimens in the low humidity group, which remained at 70% humidity, showed insignificant mass increases of only 0.01 mg/cm^2 during this period. The control specimen, which was also exposed to 100% humidity, increased in mass by only 0.14 mg/cm^2 during the same period. These curves show that the vertical location during the fire test had no significant effect on the ensuing corrosion, probably because the smoke density varied only slightly with height during this test.

The macroscopic corrosion features for the HY80 steel specimens are shown in Figure 9. The circular arc striations on the surfaces of all the specimens are due to the machining process used to prepare the specimens. Very little rust is visible on the controls and the low humidity specimens, but many large rust patches are visible on the high humidity specimens. The rust tends to follow the machining grooves on these specimens. The amount of corrosion experienced by the high humidity specimens in Test W-11 is actually relatively small and is not expected to significantly reduce the tensile strength of these specimens.
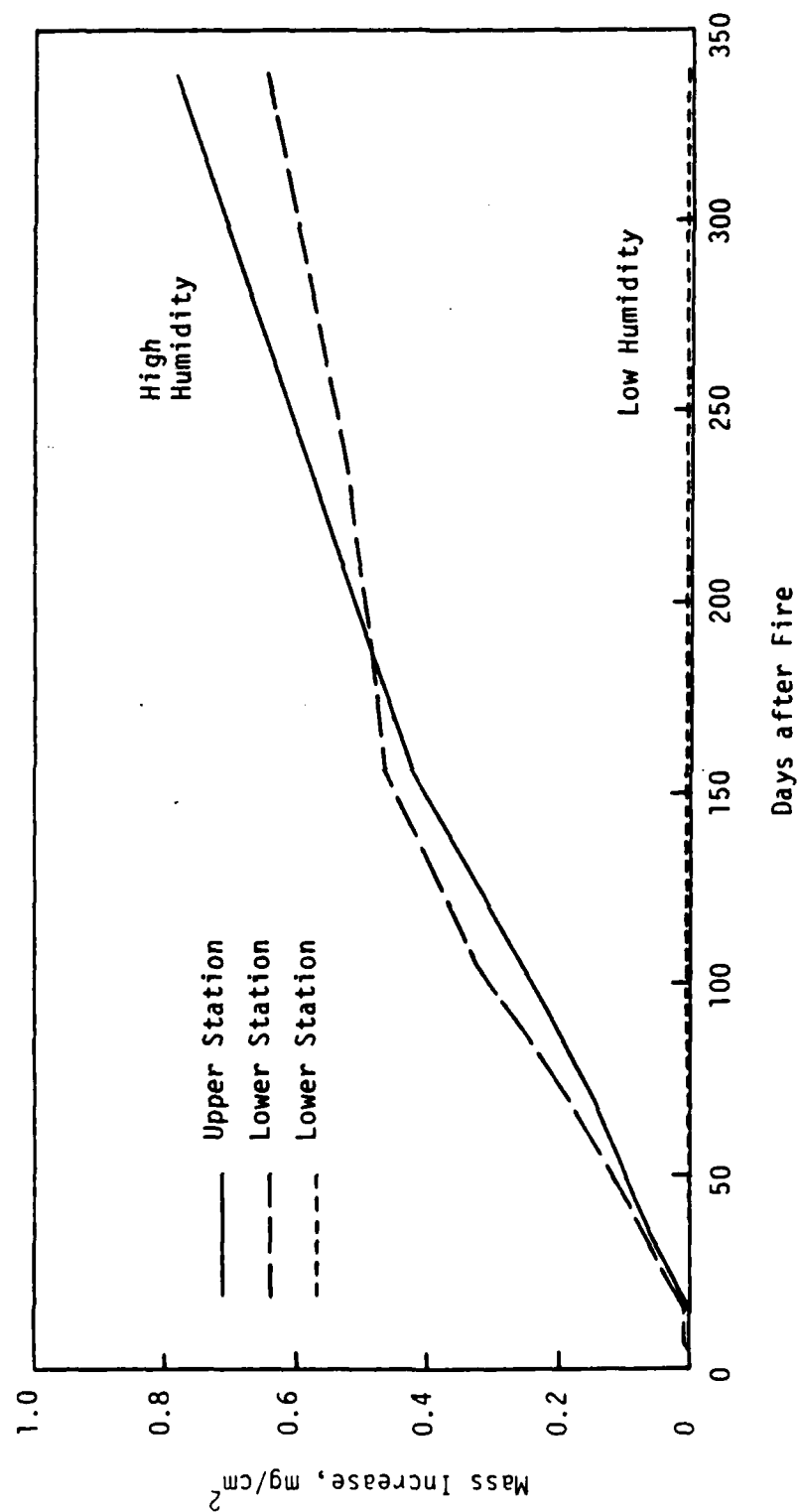
Figure 8. Mass Increases Due to Corrosion for HY80 Steel for Test W-11.
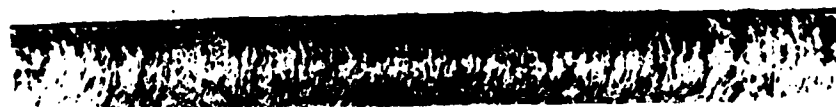
Controls

Upper
Station

Lower
Station

Low Humidity

Upper
Station

Lower
Station

High Humidity

Figure 9.   Macroscopic Corrosion Features for HY80
Steel for Test W-11.

Type 304 Stainless Steel

The gravimetric data for the #304 stainless steel specimens are plotted in Figure 10. The weight changes are extremely small, and they are near the limit of sensitivity of the analytical balance. The control specimen also experienced similar weight changes in the high humidity environment. These results show that the stainless steel did not experience measurable corrosion from exposure to the combustion products generated in Test W-11, regardless of the vertical location in the fire compartment or the post-fire humidity conditions. Macroscopic and microscopic examination of the specimens also revealed no interference tints or other evidence of corrosion.

Brass

The mass increases for the brass specimens exposed to the combustion products generated in Test W-11 are presented in Figure 11. For both stations a mass increase of about .005 mg/cm^2 occurred during the first week after the fire under 70% relative humidity, but little further mass increase occurred for the low humidity group during the remaining 230 days of the corrosion assessment period. The mass increases were only slightly greater for the specimens from the lower station which were stored at 100% humidity. During the first 25 days of the high humidity phase, the specimens from the upper station increased in mass by an additional .006 mg/cm^2, but little further change occurred during the rest of the post-fire period. This initial mass increase in the 100% humidity environment probably resulted from the absorption of moisture by combustion products deposited on the surface of these specimens. The mass increases for the control specimen (100% humidity) were
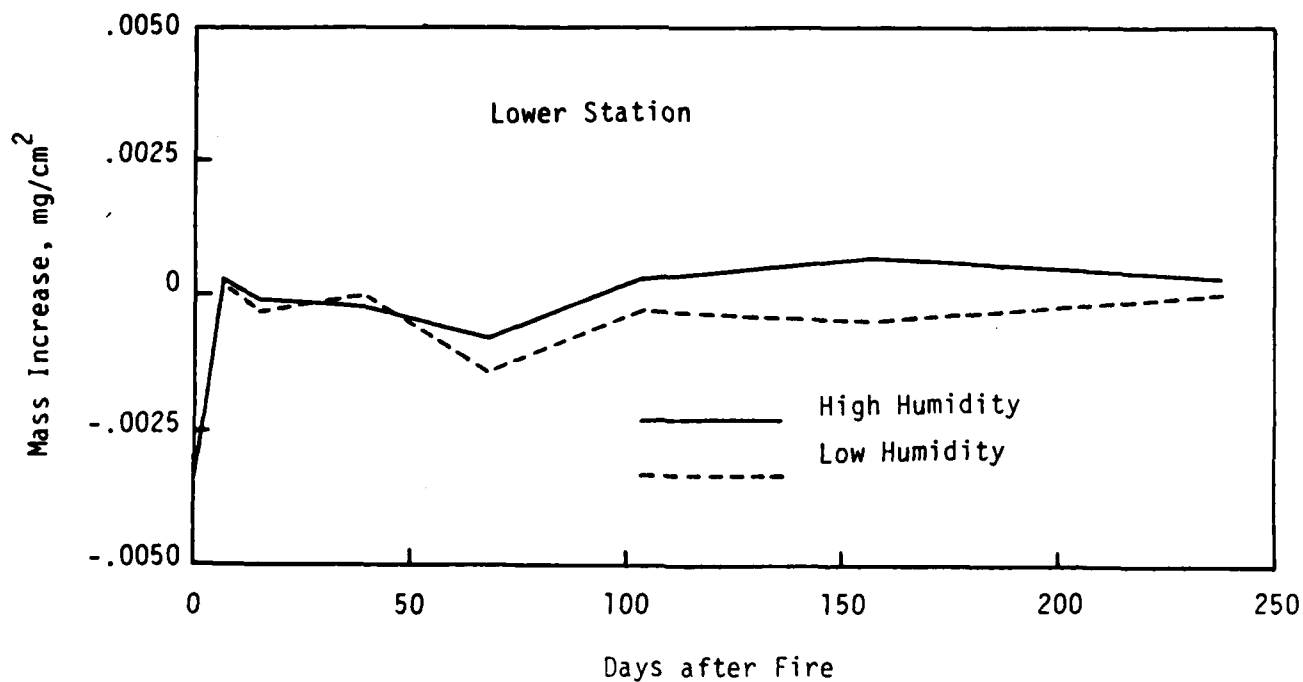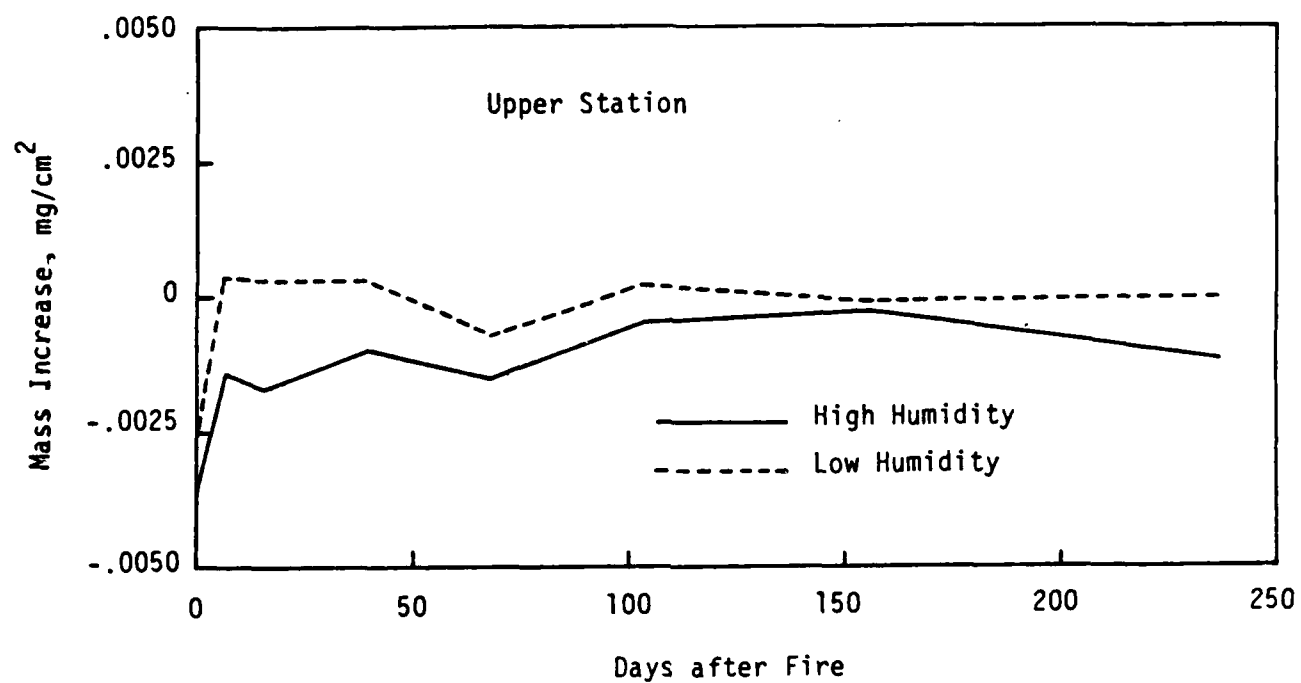
28

Figure 10. Mass Increases Due to Corrosion for Type 304 Stainless
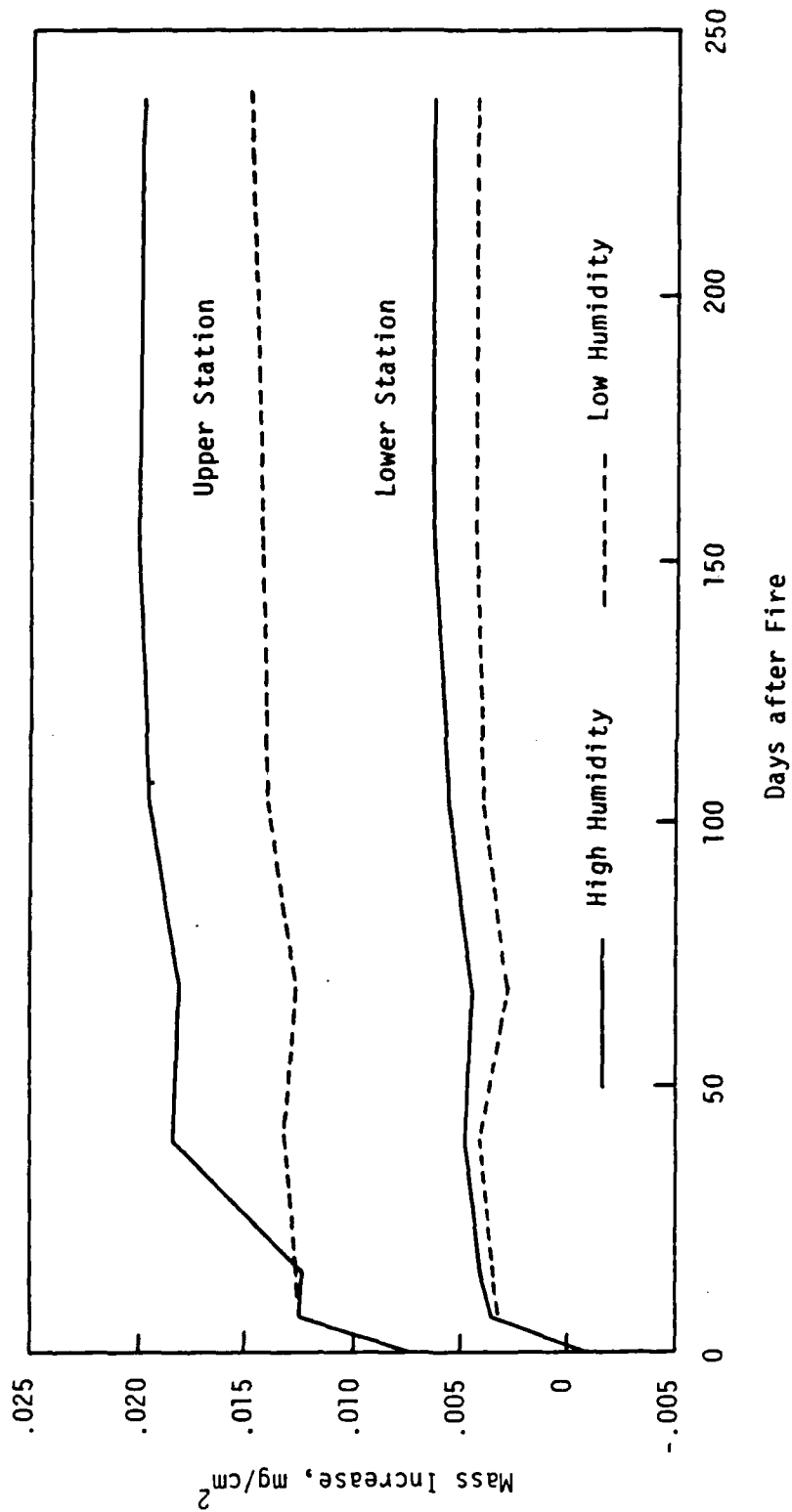Steel for Test W-11.

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Figure 11. Mass Increases Due to Corrosion for Brass for Test W-11.

all slightly less than those for the low humidity specimens from the lower station.

At the end of the post-fire period the brass specimens from Test W-11 exhibited evidence of thin film corrosion in the form of tarnish and interference tints. The specimens from the upper station were dull. with the low humidity specimens having a bluish tint while the high humidity specimens were close to the normal brass color. The specimens from the lower station were surprisingly bright with the low humidity specimens slightly deeper in color than normal brass. The specimens from the high humidity group at this location exhibited strong and brilliant interference tints ranging from golden-orange over most of the surface to magenta and indigo at the edges. The variations in color indicate variations in the thickness of the films, with thickness increasing as color progresses from yellow through magenta to blue (Ref. 2). The mass increase due to thin films yielding interference tints is very small, since they are only 0.2-0.4 μm thick (for first order colors), which is consistent with the gravimetric data presented in Figure 11.

Monel 400

The gravimetric data for the Monel 400 specimens exposed to the combustion products generated in Test W-11 are plotted in Figure 12. The specimens from both stations increased in mass by about 0.008 mg/cm^2 during the first week after the fire (70% humidity environment), and those which remained at low humidity exhibited much smaller additional mass increases during the remaining 230 days of the observation period. The specimens in the high humidity group gained an additional .008 mg/cm^2 of mass during the first 25 days after the humidity was increased to 100%, but showed little further change in mass at the end of the post-fire period. As with the brass
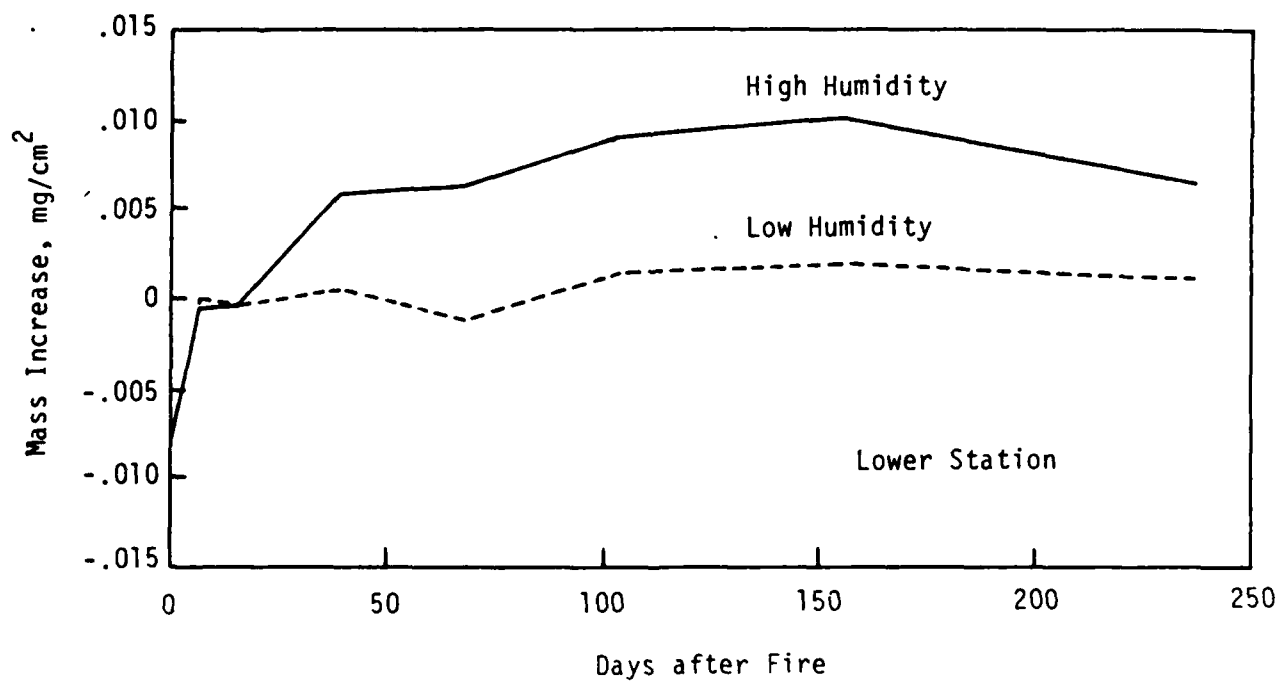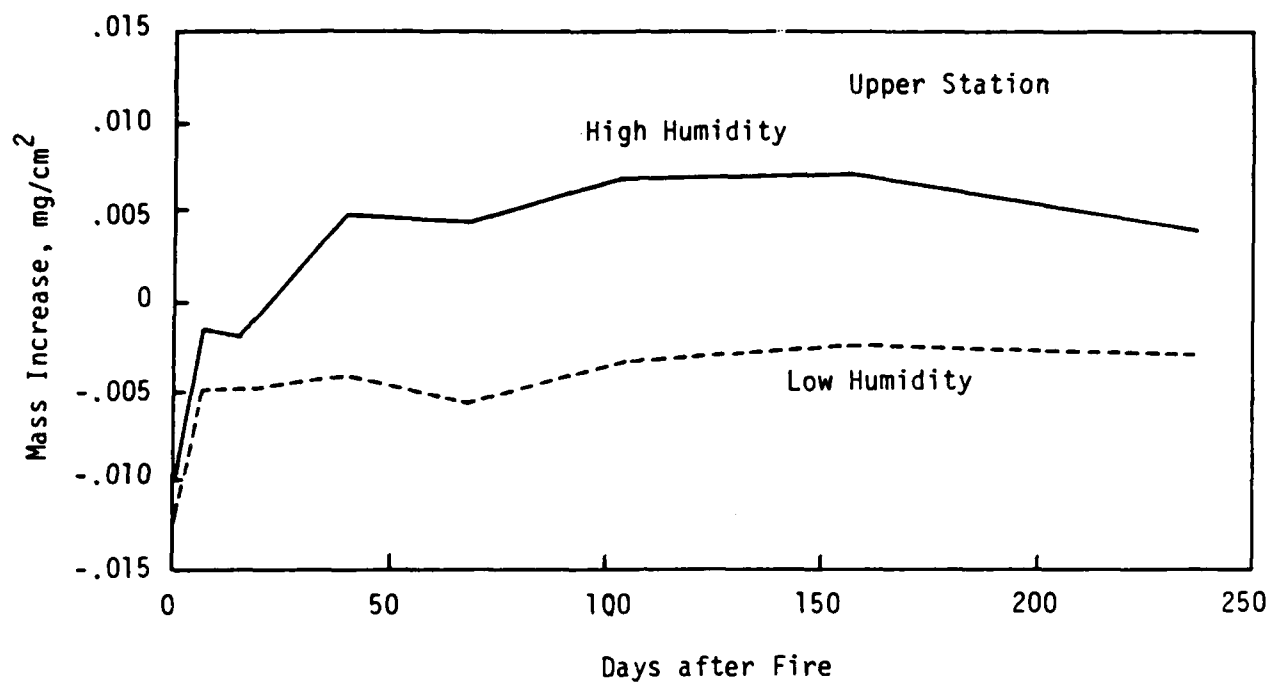
31

Figure 12.   Mass Increases Due to Corrosion for Monel 400 for Test W-11.

specimens, the mass increases for the high humidity group of Monel 400 speci-
mens are attributed to absorption of moisture by the deposited combustion
products. The control specimen, which was also exposed to high humidity,
exhibited mass changes similar to those of the low humidity specimens from the
lower station. Examination of the Monel 400 specimens at the end of the
post-fire assessment period revealed no visible evidence of corrosion.

Summary

The gravimetric results of Test W-11 are summarized in Table 4. Of the
four target materials exposed to the combustion products generated by burning
MIL-C-24640 and 24643 cables in Test W-11, only the HY80 steel experienced
significant corrosion, in the form of rust, during the high humidity period
(15-237 days). The mass increases due to corrosion for HY80 steel specimens
exposed to the smoke and stored under 100% relative humidity were five to six
times greater than those for the control specimen, which was not exposed to
the smoke. Furthermore, the mass increases for the high humidity specimens
were roughly 60 times greater than those for the low humidity specimens during
the same period.

None of the type 304 stainless steel, brass, or Monel 400 specimens
experienced significant corrosion due to exposure to the smoke generated by
the MIL-C-24640 and 24643 cables in Test W-11, regardless of the vertical
location in the fire test compartment or the post-fire humidity conditions.

Table 4.   Incremental Weight Gains for Test W-11

Material	Station	Weight Increase During Period (mg/cm^2)		
		Low Humidity Period (0 - 15 days)	High Humidity Period (15 - 237 days)	
		Both Groups	L. H. Group	H. H. Group
HY80 Steel	1	0.005	0.014	0.588
	2	0.008	0.007	0.520
#304 Stainless Steel	1	0.0025	- 0.0003	0.0005
	2	0.0033	0.0003	0.0004
Brass	1	0.0047	0.0023	0.0075
	2	0.0047	0.0009	0.0022
Monel 400	1	0.0082	0.0019	0.0058
	2	0.0077	0.0015	0.0068

RESULTS OF TESTS W-13 AND W-13A

The metal specimens in Tests W-13 and W-13A were exposed to the combustion products generated by the MIL-C-915E, Amend. 2 cables. In Test W-13 the cables failed to ignite and the metal coupons were exposed briefly to the light smoke produced by smoldering combustion of the cable jacket material. In Test W-13A, which was conducted the next day, the cables ignited and the specimens were exposed to the dense, sooty smoke produced by flaming combustion of the cables. In the following discussion the Test W-13 specimens refer to those removed from the fire test compartment after Test W-13 and thus exposed only to the smoke and gases due to nonflaming combustion. The Test W-13A specimens refer to those left in the fire test compartment after Test W-13 which thus received a cumulative exposure to both the nonflaming combustion products from Test W-13 and the flaming combustion products from Test W-13A.

The initial mass increases for the W-13 specimens are given in Table 5, while the corresponding mass increases for the W-13A specimens are given in Table 6. For Test W-13 the initial weight gains for stainless steel, brass, and Monel were small, ranging from about 0.01 to 0.05 mg/cm^2. For the stainless steel and Monel the initial mass increases probably represent simply deposition of particulates on the specimen surfaces, with little or no mass increase due to corrosion. For these two materials the smoke deposition was significantly greater at the lower station (2) than at the higher station (1). For the brass specimens at the upper station, the higher initial mass increase is likely due to corrosion, since these specimens exhibited a dull tarnished appearance. In contrast, the initial mass increases for the HY80 steel

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Table 5. Initial Weight Gains for Test W-13

Material	Station	Average Weight Increase (mg)	Weight Increase per Unit Area (mg/cm^2)
HY80 Steel	1	3.7 ± .1	0.143
	2	12.5 ± .1	0.486
#304 Stainless Steel	1	0.35 ± .01	0.0092
	2	0.58 ± .01	0.0151
Brass	1	2.01 ± .01	0.0522
	2	0.45 ± .01	0.0117
Monel 400	1	0.48 ± .01	.0237
	2	0.95 ± .01	.0468

specimens were roughly ten times larger than those for the other materials, and they were predominantly due to corrosion as indicated by the light coating of rust seen on these specimens. The initial mass increases due to corrosion for the HY80 steel coupons at the lower station were about four times greater than those for the upper station coupons, a result consistent with the larger deposition of corrosive combustion products at the lower station obtained for the other more corrosion resistant materials. The period of time during which the initial corrosion occurred for the W-13 specimens was slightly longer than one day, since the W-13 and W-13A specimens were both weighed after Test W-13A.

The initial mass increases shown in Table 6 for the W-13A specimens include both the contributions for Test W-13 (which should be similar to those presented in Table 5) and the additional contributions due to Test W-13A. For the stainless steel and Monel coupons, the initial mass increases were again primarily due to surface deposition of smoke particulates. At the upper station the mass of particulates deposited on these specimens during Test W-13A was about 18 times that deposited during Test W-13 alone. The corresponding ratio for the lower station coupons was much less, only about 2.7, which indicates a pronounced stratification of the smoke in the fire compartment during Test W-13A with much greater smoke densities at the upper station. For the brass coupons the average initial mass increases were much larger, nearly 5 mg/cm^2 at the upper station and nearly 0.3 mg/cm^2 at the lower station. The upper station brass coupons were coated with a very black, apparently wet, smooth deposit as if a hygroscopic corrosion product was formed on the surface of the brass which attracted large quantities of water from the environment. Assuming similar quantities of deposited combustion

Table 6. Initial Weight Gains for Test W-13A

Material	Station	Average Weight Increase (mg)	Weight Increase per Unit Area (mg/cm^2)
HY80 Steel	1	16.1 ± .1	0.629
	2	18.1 ± .1	0.707
#304 Stainless Steel	1	6.30 ± .01	0.164
	2	2.14 ± .01	0.0557
Brass	1	188.4 ± .1	4.91
	2	11.13 ± .01	0.290
Monel 400	1	9.42 ± .01	0.465
	2	3.48 ± .01	0.172

products, the amount of water adsorbed by the upper station brass coupons accounts for at least 90% of their total initial mass increase. About 60% of the much smaller mass increases for the lower station brass specimens was probably due to water adsorption. The HY80 steel coupons experienced more modest additional mass increases during the W-13A test. At the upper station the mass increase of the HY80 steel during Test W-13A was about 3.5 times the mass increase during Test W-13 alone, while at the lower station the mass increment increased by only 45% during Test W-13A. These mass increases for the HY80 steel during Test W-13A were largely due to the heavy, fluffy depos-· its of sooty black and grey material observed on these specimens.

During the post-fire corrosion assessment period, which lasted 190 days (295 days for HY80 steel), the mass increase due to corrosion was determined by periodic weighings. The results for both W-13 and W-13A coupons are presented as graphs of mass increase due to corrosion versus elapsed time (in days) after the W-13A test. In presenting the gravimetric data for the W-13 specimens, the extra day is neglected. At the conclusion of the assessment period macroscopic photographs were made of the surface deposits and corrosion products. Finally the coupons were cleaned to remove loosely adhering combustion products and corrosion products and weighed to determine the mass of metal lost due to corrosion. The results are discussed separately for each of the materials in the remainder of this section.

HY80 Steel

Gravimetric data for the HY80 steel specimens are presented in Figures 13 and 14 for Test W-13 (nonflaming) and in Figures 15 and 16 for Test W-13A

(flaming). In Figures 13 and 15 the mass increase per unit surface area $(\Delta m/A)$ is plotted versus elapsed time. This data includes the initial mass increases shown in Tables 5 and 6 as the values at time zero. Figures 14 and 16 display the average corrosion rates in mg/cm^2 per day during the time intervals between weighings, where the elapsed time for each plotted point is midway between the times for the corresponding weighings.

The curves of mass increase versus time for a given humidity group are qualitatively similar for both the W-13 (nonflaming) and the W-13A (flaming) specimens and for both upper and lower stations. For a given test and vertical location, however, these curves indicate the dramatic effect of ambient humidity in accelerating the corrosion process for HY80 steel. For example, consider the Test W-13A (flaming) specimens from the lower station (Figure 15, lower graph) for which the largest mass increases were obtained. During the first 20 days after the fire, when both humidity groups were at about 70% humidity, only modest mass increases (about 2.2 mg/cm^2) were obtained. After the humidity was increased to nearly 100%, the specimens in the high humidity group increased steadily in mass, reaching $\Delta m/A$ in excess of 16 mg/cm^2 at the end of the corrosion assessment period. The specimens in the low humidity group, which remained at 70% humidity, showed very little additional increase in mass, reaching $\Delta m/A$ of only about 3 mg/cm^2. The control specimen, which was also exposed to 100% humidity, increased in mass by only about 0.3 mg/cm^2 during the same period. The specimens from the upper station for Test W-13A (Figure 15, upper graph) exhibited slightly lower mass increases due to corrosion than those from the lower station, in spite of the much greater smoke density which prevailed at the upper station during Test W-13A. The W-13 specimens, which were exposed only to the products of smoldering
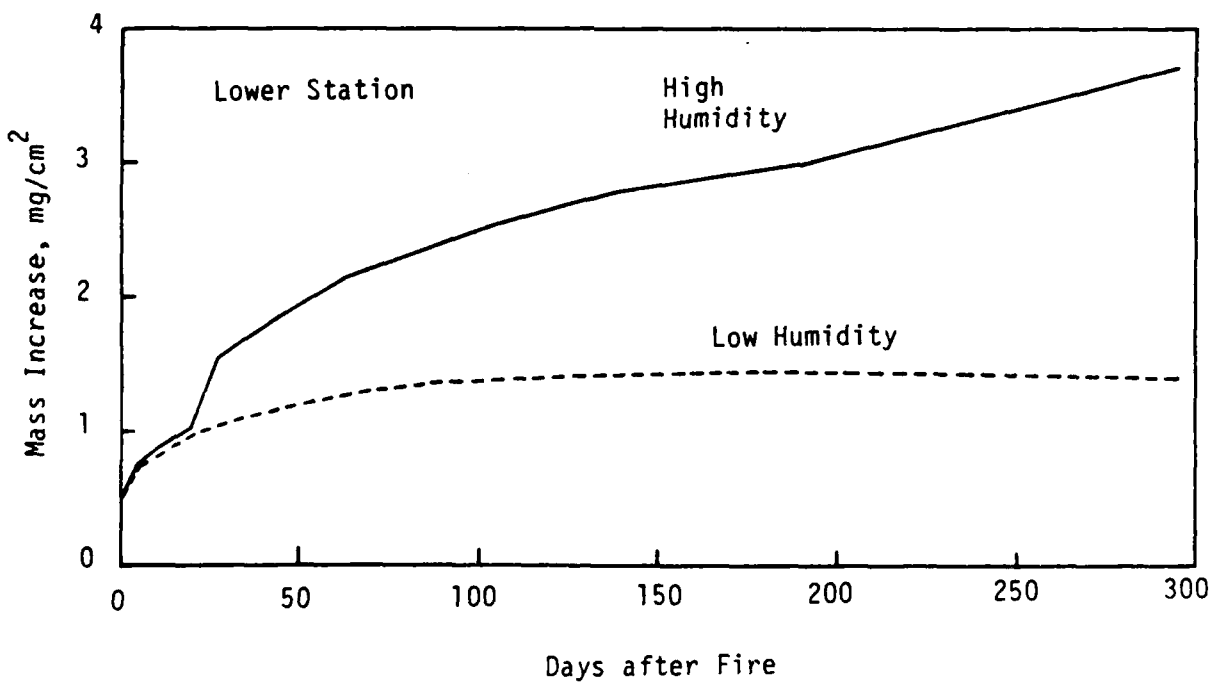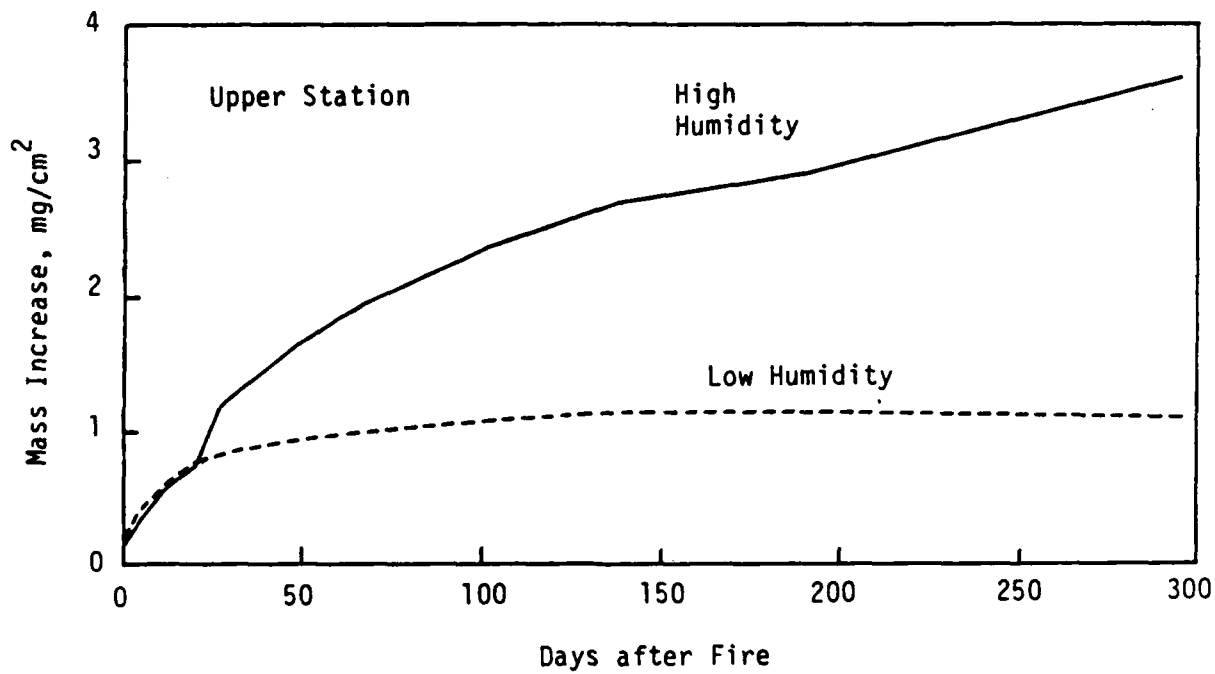
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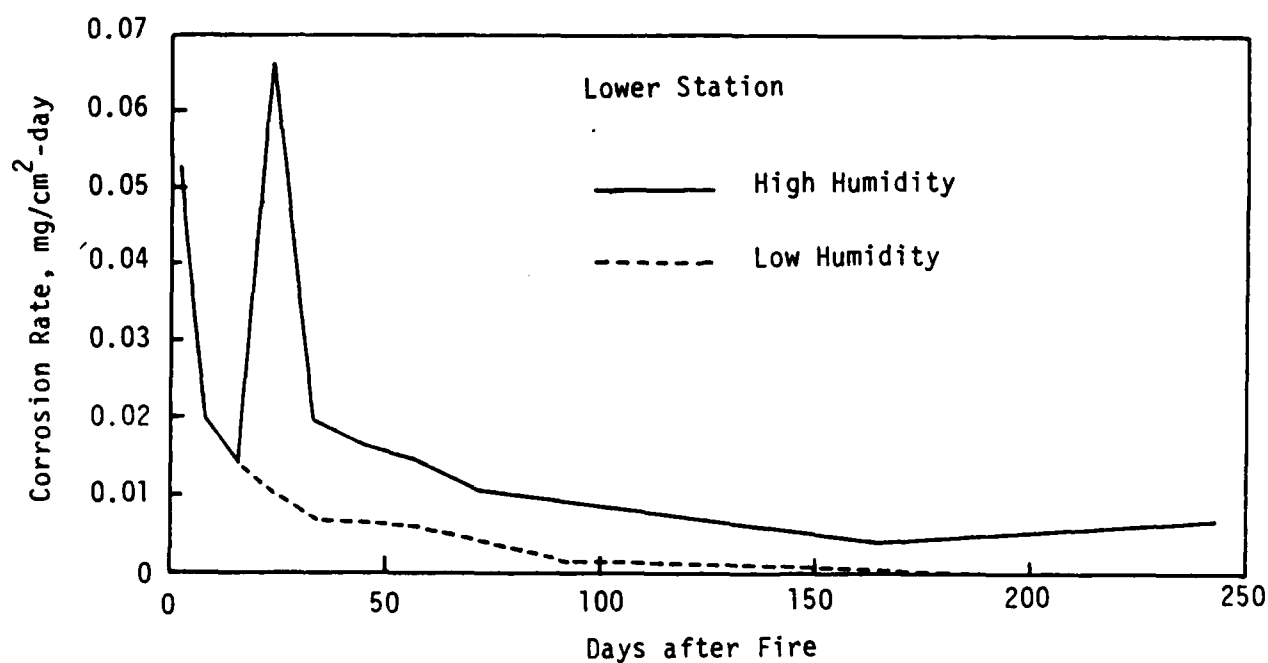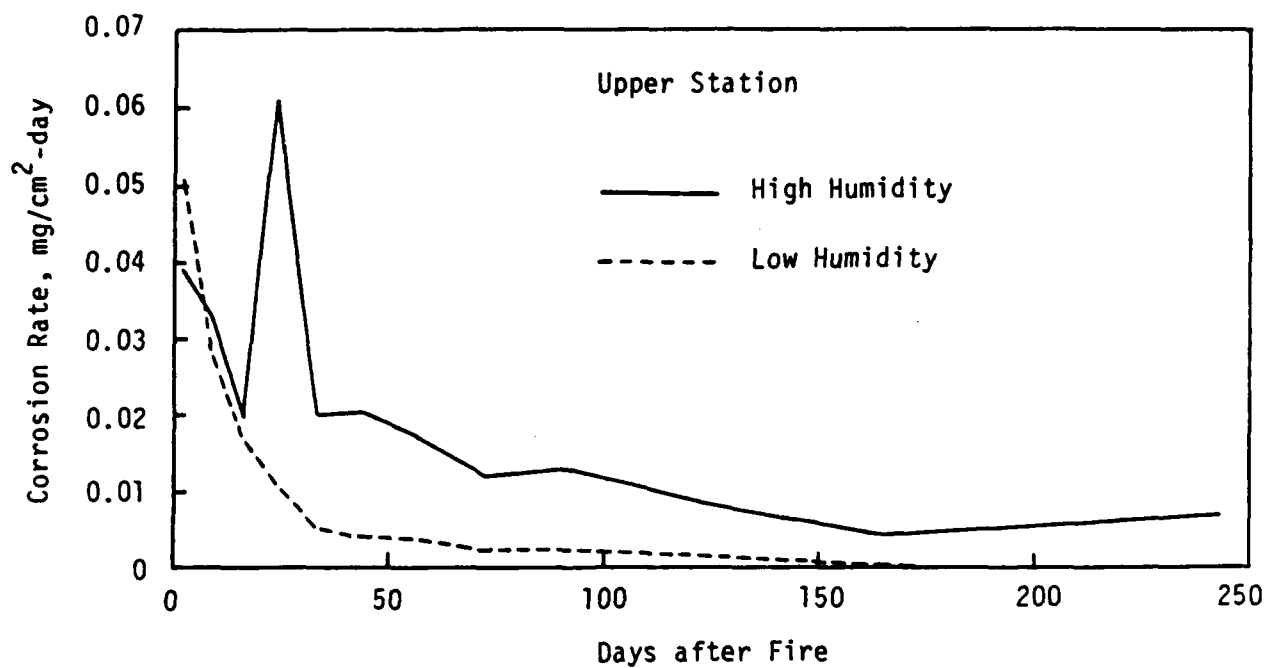Figure 13. Mass Increases due to Corrosion for HY80 Steel for Test W-13 (Nonflaming).

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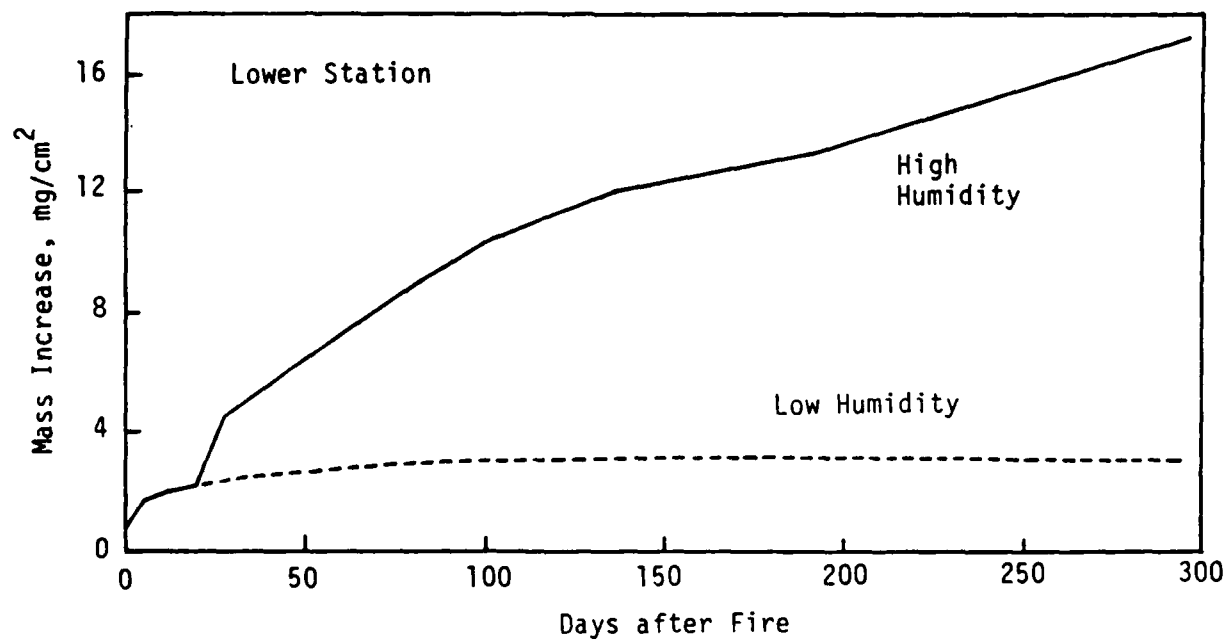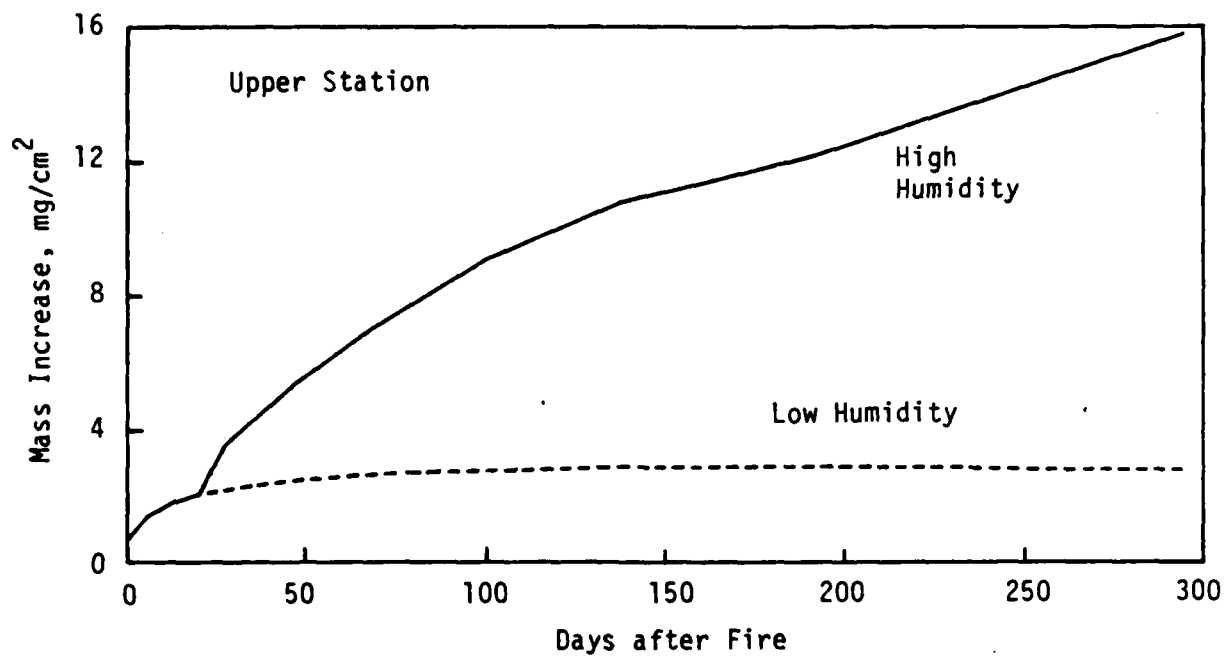Figure 14. Corrosion Rates for HY80 Steel for Test W-13 (Nonflaming).

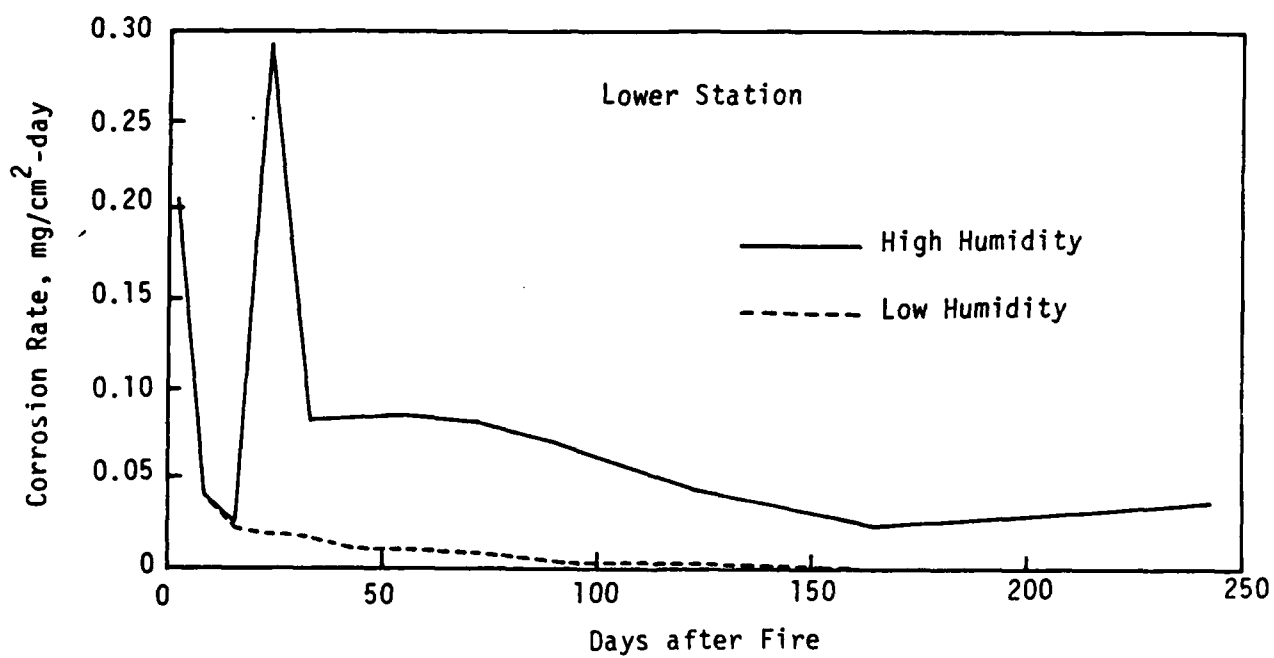Figure 15. Mass Increases due to Corrosion for HY80 Steel for Test W-13A (Flaming).
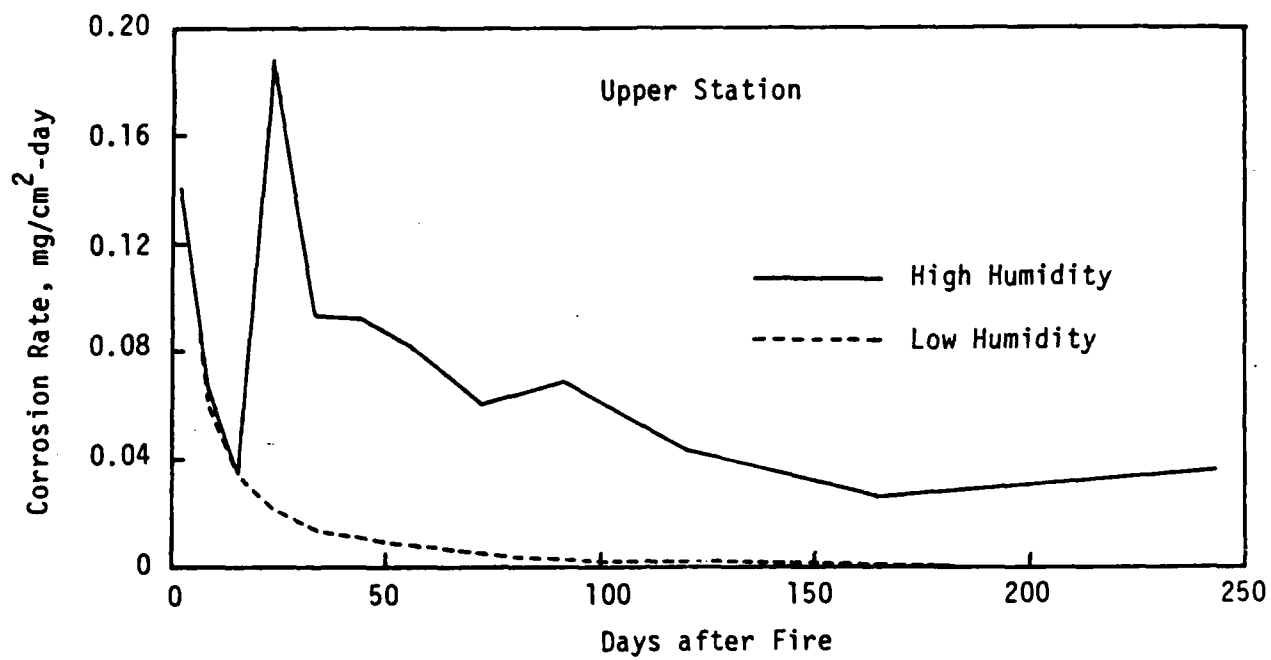
Figure 16.   Corrosion Rates for HY80 Steel for Test W-13A (Flaming).

combustion, experienced much smaller mass increases than the corresponding W-13A specimens (Figure 13). These $\Delta m/A$ values ranged from about 22% (high humidity) to about 42% (low humidity) of the corresponding values for Test W-13A. For the W-13 specimens the effect of vertical location upon the mass increases due to corrosion was also insignificant.

The corrosion rates displayed in Figures 14 and 16 were also qualitatively similar for all specimens in a given humidity group, regardless of vertical location or test. For the typical case of the lower station Test W-13A specimens (Figure 16, lower graph), both humidity groups experienced a rapidly declining corrosion rate during the first 20 days at 70% humidity. For the low humidity group specimens the corrosion rate essentially reached zero after 150 days. For the high humidity group specimens, however, the rate of mass increase soared to about 0.3 mg/cm^2 per day during the first eight days of exposure to 100% humidity conditions. During the next 11 day period the corrosion rate dropped to only 0.08 mg/cm^2 per day and gradually declined thereafter. It is suspected that the large peak in mass increase rate upon initiation of the high humidity phase is due partially to the absorption of water by the surface deposits and the corrosion products already present. This water is eventually incorporated into the corrosion products as water of crystallization, and the subsequent mass increase rates are likely due to continued corrosion. The corrosion rates for Test W-13 (nonflaming) are all significantly smaller than the corresponding rates for Test W-13A as shown by comparing Figure 14 with Figure 16.

The macroscopic corrosion features for the HY80 steel specimens at the end of the corrosion assessment period are shown in Figures 17 and 18. The

Test W-13 (nonflaming) specimens are shown in Figure 17, where all specimens are seen to be covered with a continuous layer of rust with a rough granular texture and dark reddish brown color. The specimens from the high humidity group (lower pair) show a thicker, rougher rust layer with a lighter color than the specimens from the low humidity group (upper pair). The specimens from the upper and lower stations are virtually indistinguishable in appearance for each humidity group. For comparison the control specimen is shown in Figure 9.

Figure 18 shows the W-13A (flaming) specimens of HY80 steel. The specimens from the upper station (upper specimen in each pair) are seen to be covered with a thick fluffy layer of soot, which completely obscures the underlying rust for the low humidity specimen. For the corresponding high humidity specimen some rust can be seen through breaks in the soot layer. For the specimens from the lower station (lower specimen in each pair), little soot is visible, and again a heavy rough textured coating of rust is seen. The low humidity specimen appears reddish brown with many irregular shaped flecks of much darker material. For the high humidity specimen the darker material predominates and the surface texture is rougher.

At the end of the post-fire period the W-13A HY80 steel specimens were cleaned and weighed. These specimens were cleaned in three stages. First all loosely adhering material was scraped off with a small steel spatula. Next the surfaces were rubbed vigorously with very fine steel wool (#00) to remove all but the most tightly bound corrosion products. Finally the surfaces were wiped thoroughly with tissue and methanol.

Upper
Station

Lower
Station

Low Humidity

Upper
Station

Lower
Station

High Humidity

Figure 17.   Macroscopic Corrosion Features for HY80
Steel for Test W-13 (Nonflaming).

Upper
Station

Lower
Station

Low Humidity

Upper
Station

Lower
Station

High Humidity

Figure 18.   Macroscopic Corrosion Features for HY80
            Steel for Test W-13A (Flaming).

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For the W-13A specimens from the upper station, humidity had a strong effect on the quantity and composition of the material removed during the first stage of cleaning. For the low humidity specimens, an average of about 0.4 mg/cm^2 of dark material, which was mostly soot, was removed with the spatula, leaving a reddish brown coating of rust (probably ferric oxide, Fe_2O_3). For the high humidity specimens, a black, brittle, flaky or scaly oxide layer was easily removed with the spatula leaving a similar rust layer. The mass of this loosely adherent material averaged nearly 12 mg/cm^2 for the high humidity specimens. After the rust was removed with steel wool, specimens from both humidity groups retained a tightly bonded black oxide coating, which was probably magnetite, Fe_3O_4. The total mass of material removed during cleaning was 1.53 mg/cm^2 for the low humidity group and 15.1 mg/cm^2 for the high humidity group. For the low humidity specimens the net mass increase (mass after cleaning minus mass before the fire test) was about 1.46 mg/cm^2. This represents the mass of the oxygen retained in the black oxide coating less the mass of metal contained in the corrosion products removed during cleaning. For the high humidity specimens, a much larger mass of metal was lost in the corrosion products removed during cleaning so that a net mass loss of 0.26 mg/cm^2 occurred in spite of the presence of the oxide coating.

For the W-13A lower station specimens, humidity also had a large effect on the quantity and characteristics of the corrosion products removed during cleaning. For the low humidity specimens, about 1.0 mg/cm^2 of reddish brown rust was removed with the spatula. For the high humidity specimens, about 16.4 mg/cm^2 of dark brown oxide scale mixed with rust was scraped off. After removing the remaining rust with the steel wool, the total mass of material removed during cleaning was 2.24 mg/cm^2 for the low humidity specimens and

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19.23 mg/cm^2 for the high humidity specimens. As in the case of the upper station specimens, a strongly adherent hard black oxide coating was retained on the lower station specimens after cleaning. For the low humidity group the resulting net mass increase (oxygen in oxide coating less metal lost in loose corrosion products) was 0.87 mg/cm^2. For the high humidity group, the metal lost in removed corrosion products was much larger, giving a net mass decrease of 3.86 mg/cm^2.

Type 304 Stainless Steel

The gravimetric data for the type 304 stainless steel specimens are shown in Figures 19 and 20. For the specimens exposed only to the smoke generated by nonflaming combustion (W-13), Figure 19 shows very little mass increase beyond that due to deposition of combustion products during the fire test. Most of this additional mass increase occurred during the first 30 days after the fire test, with very little change in mass thereafter. Since this post-fire mass increase was significantly larger for the high humidity group, and the specimens showed little or no visible corrosion, it is suspected that the mass increase was due to water adsorption rather than to corrosion. For the W-13A specimens (flaming), Figure 20 shows that the mass of these specimens remained essentially constant during the post-fire period of 190 days, regardless of humidity or vertical location. The small differences between the high and low humidity groups are due to variations in the amount of smoke particulates deposited on these specimens during the fire test. The control specimen increased in mass by only 0.002 mg/cm^2 during the post-fire period.
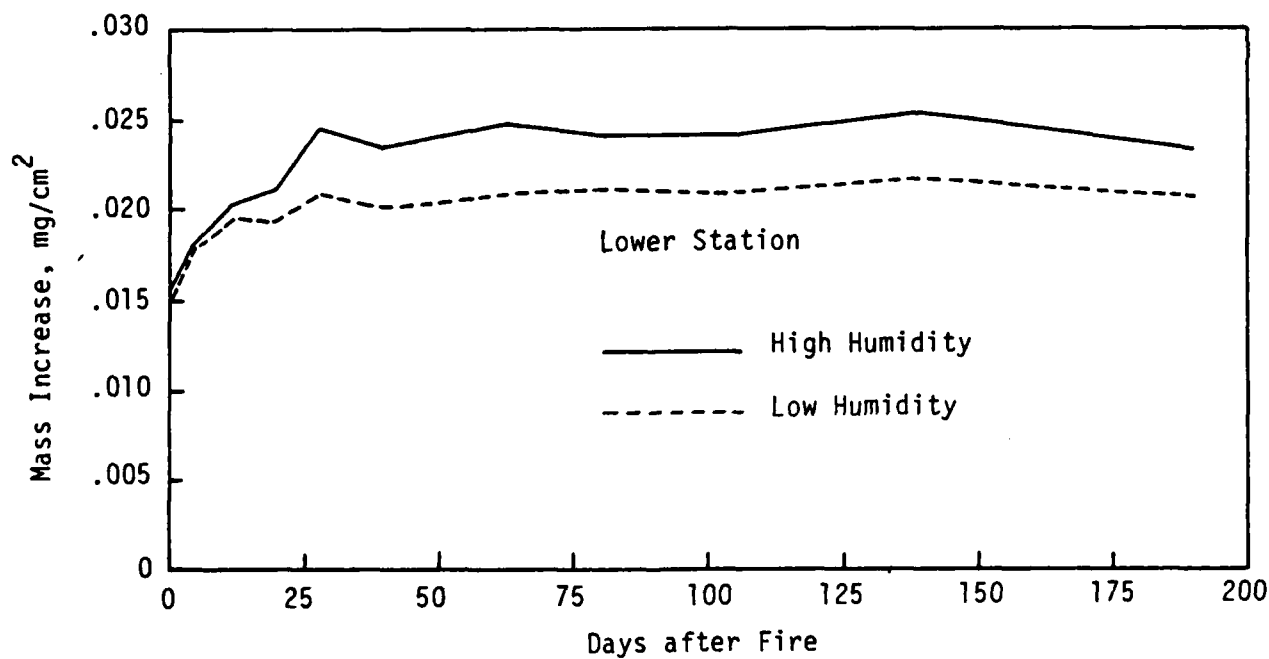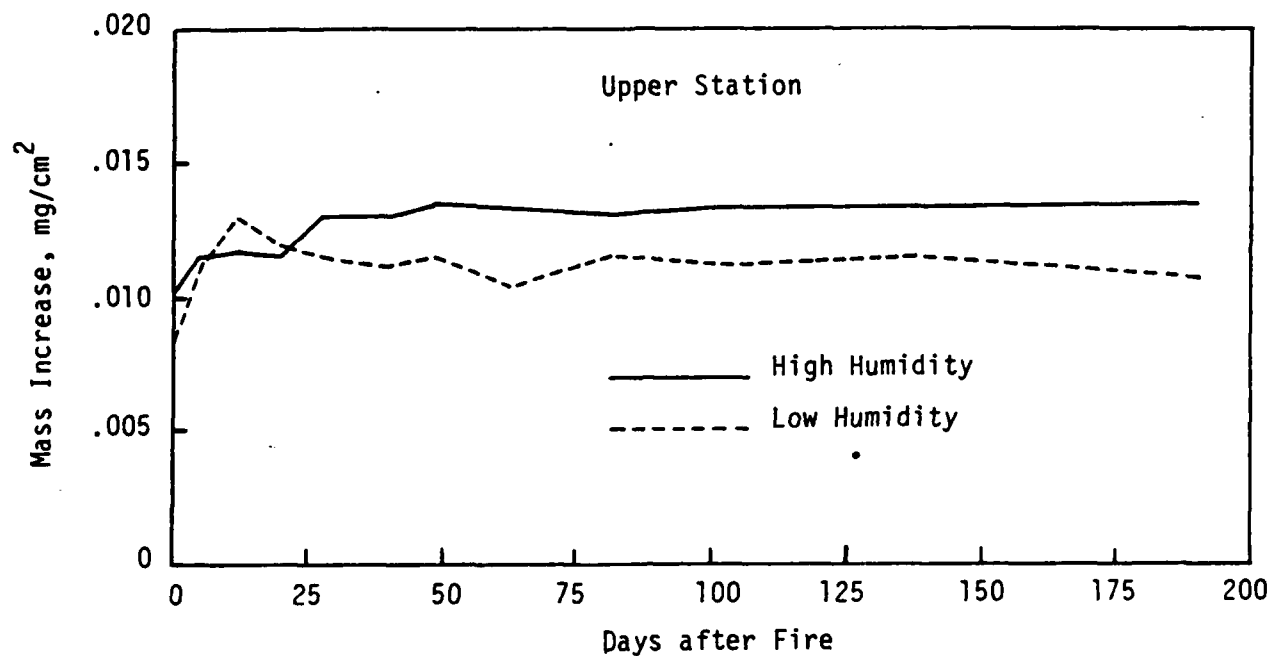
Figure 19.   Mass Increases due to Corrosion for Type 304 Stainless
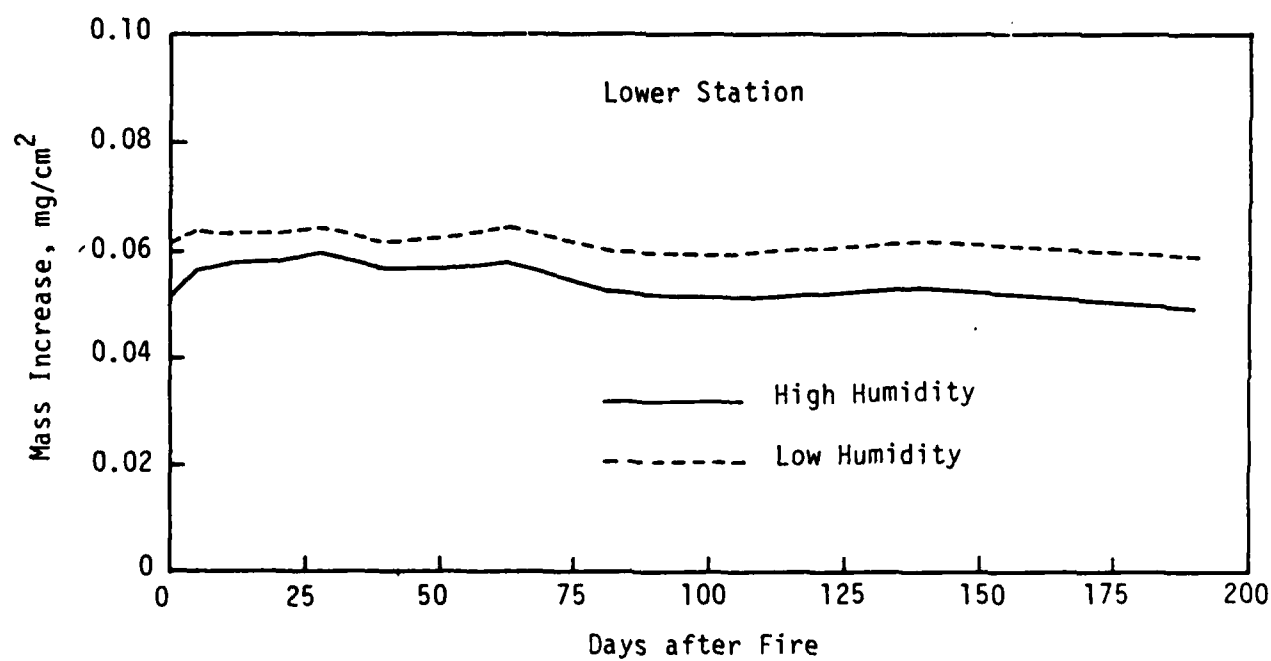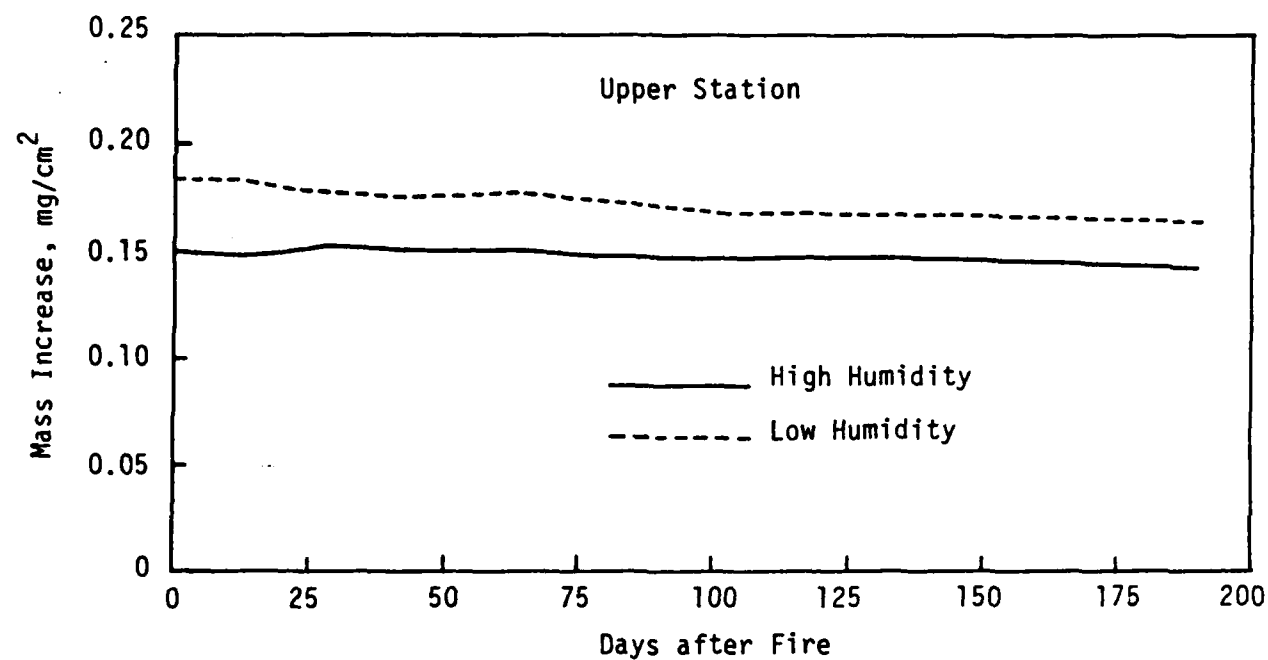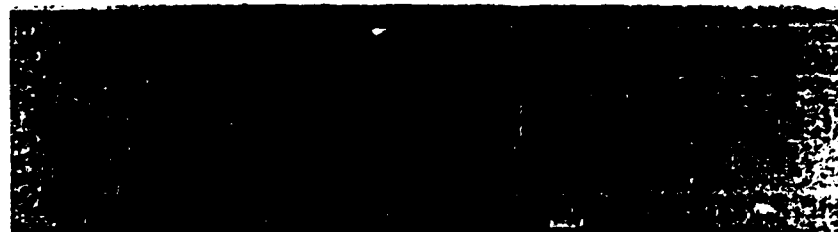   Steel for Test W-13 (Nonflaming).

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Figure 20.   Mass Increases due to Corrosion for Type 304 Stainless
Steel for Test W-13A (Flaming).

As mentioned above, the W-13 specimens (nonflaming) of stainless steel appeared clean and bright with the only visible sign of corrosion being microscopic, widely scattered specks of darker material on the specimens from the lower station. The W-13A specimens (flaming) are shown in Figure 21 along with the controls (top pair). The specimens from the upper location of both humidity groups are covered with a smooth black coating of fine soot particles sprinkled with numerous larger fluffy agglomerates of soot particles. The specimens from the lower location of both humidity groups appear very slightly tarnished, and they are sparsely sprinkled on one side with small soot agglomerates.
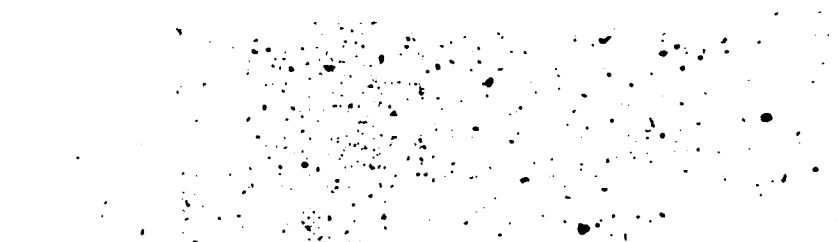
The type 304 stainless steel specimens were cleaned and weighed at the end of the corrosion assessment period. For the W-13A specimens from the upper station, the thin soot layer was gently scraped off with a razor blade, and the surface was wiped repeatedly with a tissue and methanol. For specimens of both humidity groups, about 0.1 mg/cm^2 of sooty material was removed by this procedure revealing surfaces darkened by tarnish with slight yellowish tints which were strongest at the edges. The high humidity specimens were darker and exhibited additional bluish and magenta tints, which indicate thicker oxide films (Ref. 2). The net mass increase due to the tarnish was about 0.035 mg/cm^2 for the low humidity specimens and about 0.026 mg/cm^2 for the high humidity specimens. These mass increases represent the mass of oxygen which combined with the metallic elements in the steel to form the tarnish layer. Since the gravimetric data (Figure 20) show little change in mass during the post-fire period, it is likely that the tarnish was formed by high temperature oxidation during the fire test. This would account for the insignificant effect of post-fire humidity on the corrosion process.
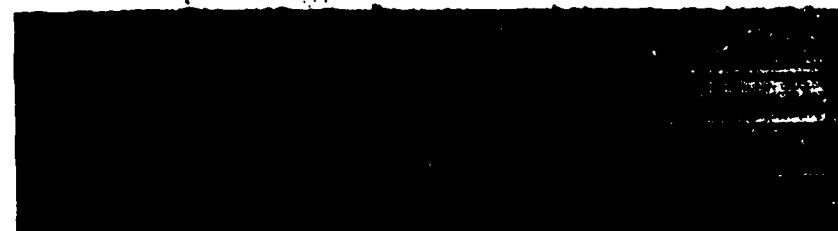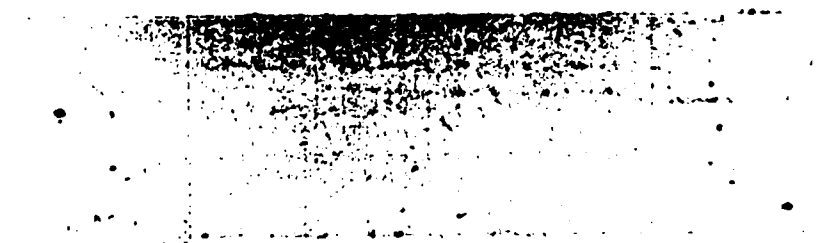
53

Controls

Upper
Station

Lower
Station

Low Humidity

Upper
Station

Lower
Station

High Humidity

Figure 21. Macroscopic Corrosion Features for Type 304
Stainless Steel for Test W-13A (Flaming).

The W-13A specimens of stainless steel from the lower station were cleaned with methanol without first using the razor blade since very little surface deposition was evident. Examination of the tissue after cleaning these specimens revealed rust stains, although rust was not visible on these specimens before cleaning. The material removed from the low humidity specimens amounted to about 0.057 mg/cm^2, while that removed from the high humidity specimens was only slightly greater, at 0.064 mg/cm^2. The metal present in the rust removed during cleaning resulted in a net mass decrease in these specimens: $\Delta m/A$ = -.006 mg/cm^2 for the low humidity group and $\Delta m/A$ = -.014 mg/cm^2 for the high humidity group. It is possible that most of this rust formed during the fire test and shortly afterward, as the gravimetric data (Figure 20) show very little variation in mass during the post-fire period.

Brass

The gravimetric data for the brass specimens are presented in Figures 22 and 23. For the W-13 specimens (nonflaming) in the low humidity group, Figure 22 shows that a slow steady increase in mass occurred during the post-fire period, but that this mass increase was small compared to the initial mass increase incurred during the fire. For the specimens in the high humidity group, an additional rapid mass increase occurred during the first eight days of the high humidity phase with very little further mass increase afterwards. As in the case of stainless steel, this increase in mass with the onset of high humidity was probably due to water adsorption. The amount of adsorbed water was about .01 mg/cm^2 regardless of the vertical location of the specimens. Figure 23 shows a similar behavior for the W-13A (flaming) specimens from the lower station, with a much larger water adsorption of about 0.12
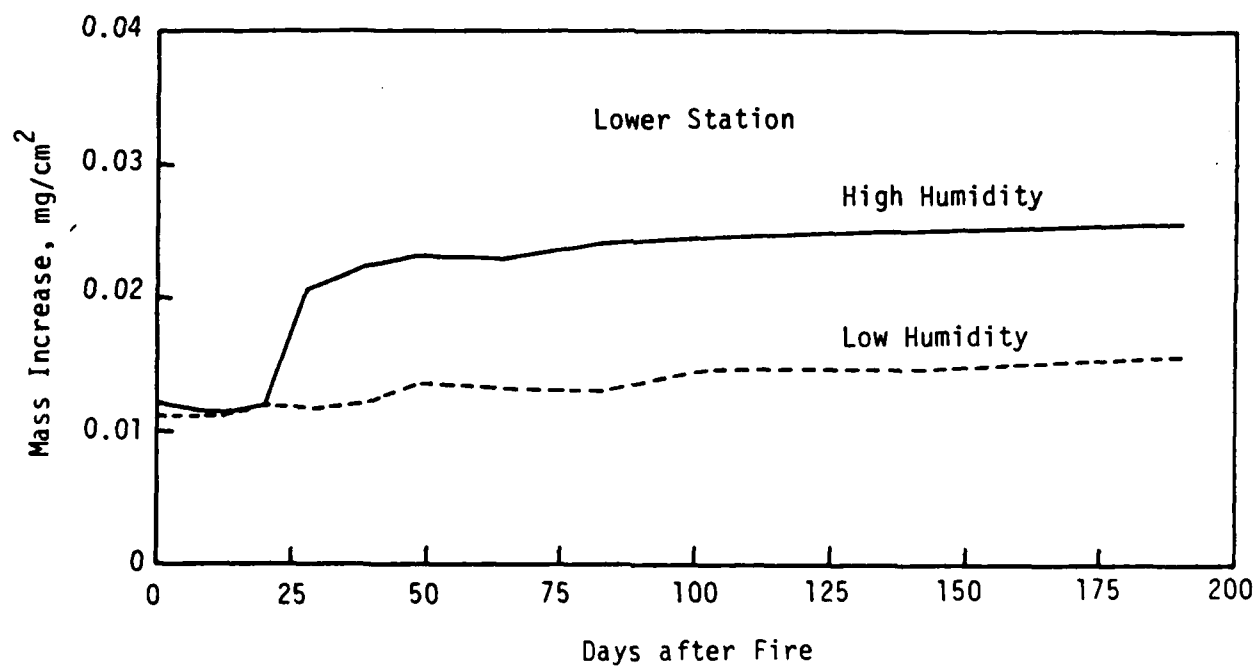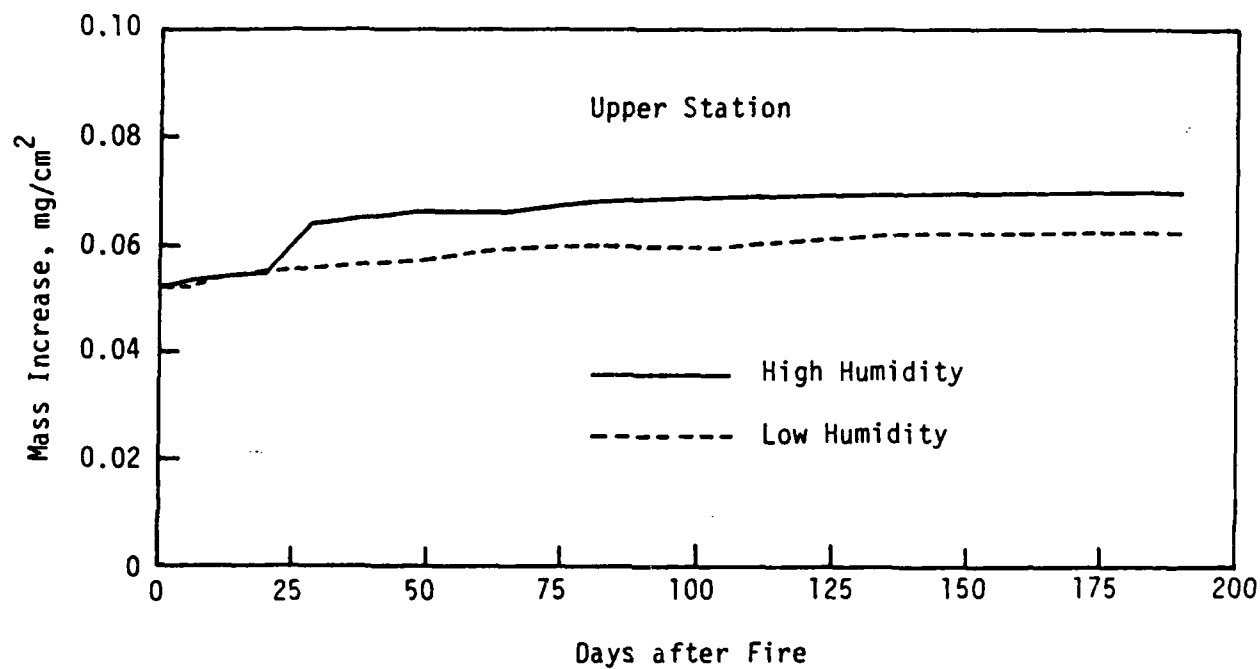
55

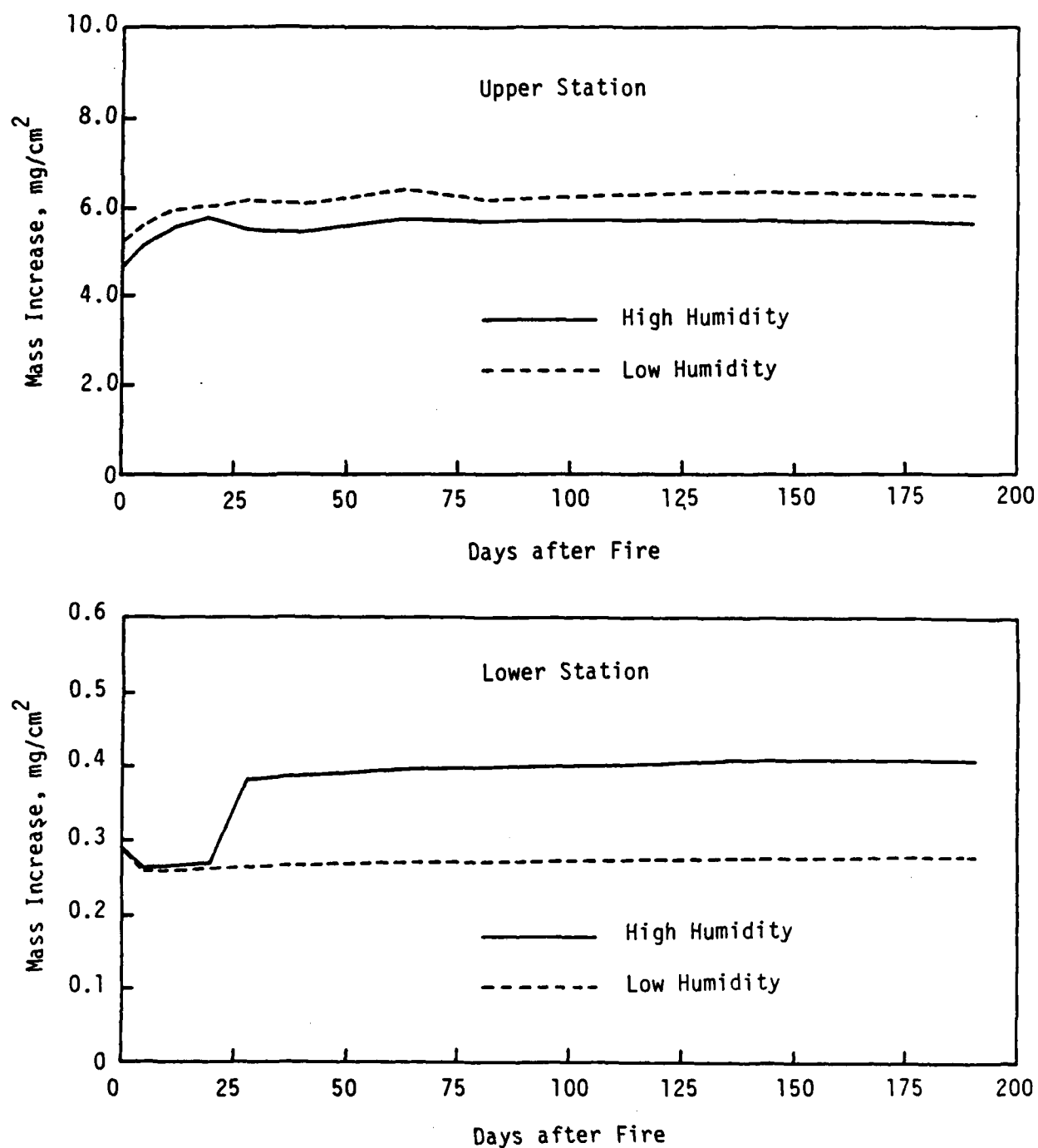Figure 22. Mass Increases due to Corrosion for Brass for Test W-13 (Nonflaming).

Figure 23.   Mass Increases due to Corrosion for Brass for Test W-13A
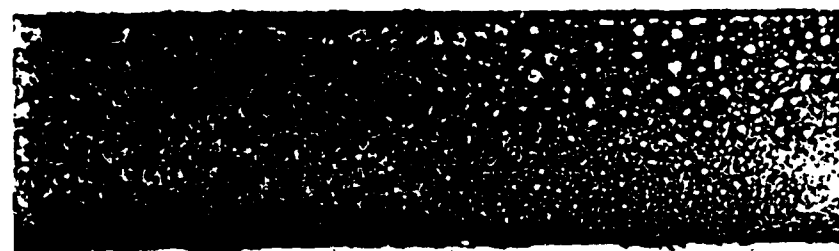   (Flaming).

mg/cm^2 during the early days of the high humidity phase. Here the water

adsorbed is about 50% of the mass of the deposited combustion products. For

the W-13A specimens of the upper station a large amount of water was adsorbed

during the fire test (nearly 5 mg/cm^2), and very little, if any, additional

water was adsorbed during the high humidity phase, although additional mass

increases of about 20% occurred during the first 20 days after the fire when

both groups were at 70% humidity. The control specimen increased in mass by

only 0.003 mg/cm^2 during the post-fire period.

The brass specimens exhibited a variety of macroscopic surface features

due to deposition and corrosion. The upper station W-13 specimens (nonflam-

ing) of both humidity groups were of a dull yellowish tarnished appearance

with pinkish and magenta interference tints. The low humidity specimens from

the lower station were covered with a darker tarnish than those from the upper

station, and they exhibited rich blue and magenta interference tints. The

high humidity specimens from the lower station were steely grey with patchy

blue interference tints. The tarnish and interference tints indicate that the

corrosion products for the W-13 brass specimens form thin films covering the

surface. These films tend to protect the surface and prevent further corro-

sion. Furthermore the mass increase due to the formation of these thin films

is very small. Thus the small, slow mass increases observed for the W-13

brass specimens is consistent with the formation of thin oxide or sulfide

films which are only slightly affected by the ambient humidity.

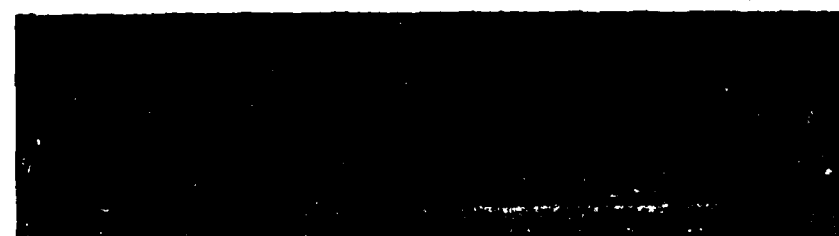The macroscopic corrosion features for the W-13A brass specimens (flam-

ing) are shown in Figure 24 at the end of the post-fire assessment period.

The specimens from the low humidity group are the middle pair in Figure 24.
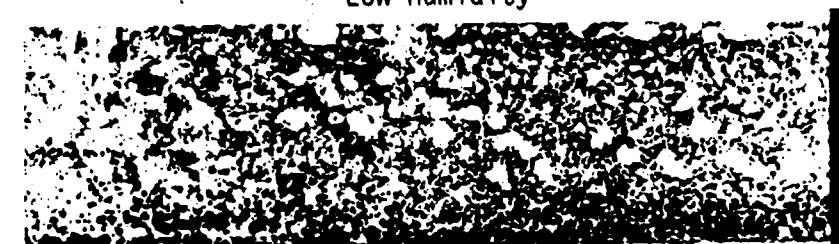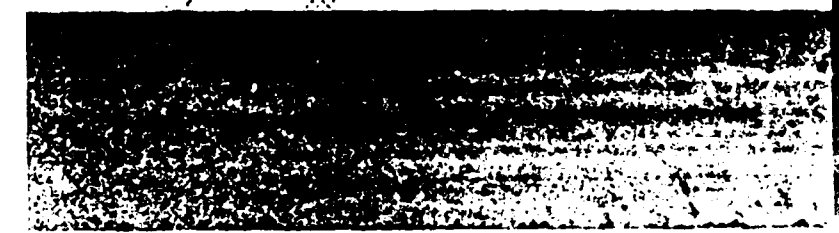
Controls

Upper
Station

Lower
Station

Low Humidity

Upper
Station

Lower
Station

High Humidity

Figure 24. Macroscopic Corrosion Features for Brass
for Test W-13A (Flaming).

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The specimen from the lower station appears to be covered with a very dark, almost black, tarnish which is sprinkled with soot agglomerates (small irregular lighter patches). The specimen from the upper station is coated with a black sooty layer which completely obscures the metal surface. The numerous small light spots appearing on the photograph of this specimen are clusters of pale bluish green crystals ranging in sizes from less than 100 microns to nearly 1000 microns across. These crystals most likely consist of copper (blue-green) and zinc salts (white) produced by reactions with acids (probably HCl) in the combustion products. The corresponding high humidity specimens are the lower pair shown in Figure 24. The lower station coupon is covered with a dark, purplish grey tarnish possibly with some soot. The specimen from the upper station is almost completely encrusted with masses of blue-green copper salt and white zinc salt crystals (light areas in the photograph), indicating that the high humidity greatly enhanced the corrosion of the brass by reactions with acidic combustion products present in the sooty layer. Since these reactions usually involve water of crystallization, this may account for the mass increases during the early phase of the post-fire period. For comparison the control specimens are included in Figure 24 as the upper pair. Although they appear dark in the photograph, they are actually the bright shiny yellow color characteristic of polished brass.

At the end of the corrosion assessment period most of the brass specimens were cleaned and weighed. The W-13A specimens from the upper station, which were heavily encrusted with corrosion products, were first scraped with a new razor blade, then rubbed with fine steel wool (00), and finally wiped several times with tissue and methanol. This process removed about 1.8 mg/cm^2 of material from the low humidity specimens and about 4.1 mg/cm^2 from the high

humidity specimens. The material removed appeared to be a mixture of soot and copper and zinc salt crystals. These specimens, after cleaning, retained a hard, black, rough coat over their entire surfaces, except for a few small spots of exposed bright metal. The high humidity specimens also retained some copper and zinc salt crystals on their surfaces. For the low humidity specimens about 3.5 mg/cm^2 of material remained on the surfaces after cleaning, while only 2.0 mg/cm^2 remained on the high humidity specimens. Since the cleaning process was the same for both humidity groups, it appears that the corrosion products on the high humidity specimens consisted of a greater proportion of salts which were more easily removed.

For the W-13A brass specimens from the lower station, very little material could be removed with the razor blade. After rubbing with fine steel wool and cleaning with methanol, a dark olive green glossy tarnish remained with a few small irregularly shaped spots and patches of bare metal. This process removed about 0.29 mg/cm^2 of material from the low humidity specimens, leaving these specimens at nearly their original weight. For the high humidity specimens, about 0.37 mg/cm^2 of tarnish was removed leaving about 0.06 mg/cm^2 on the surface.

Monel 400

The mass increases during the post-fire period for the Monel 400 specimens are shown in Figures 25 and 26. For the low humidity W-13 specimens (nonflaming), Figure 25 shows only a very small increase in mass (less than 0.01 mg/cm^2) beyond that incurred during the fire due to deposition of combustion products. For the high humidity specimens from the lower station, an
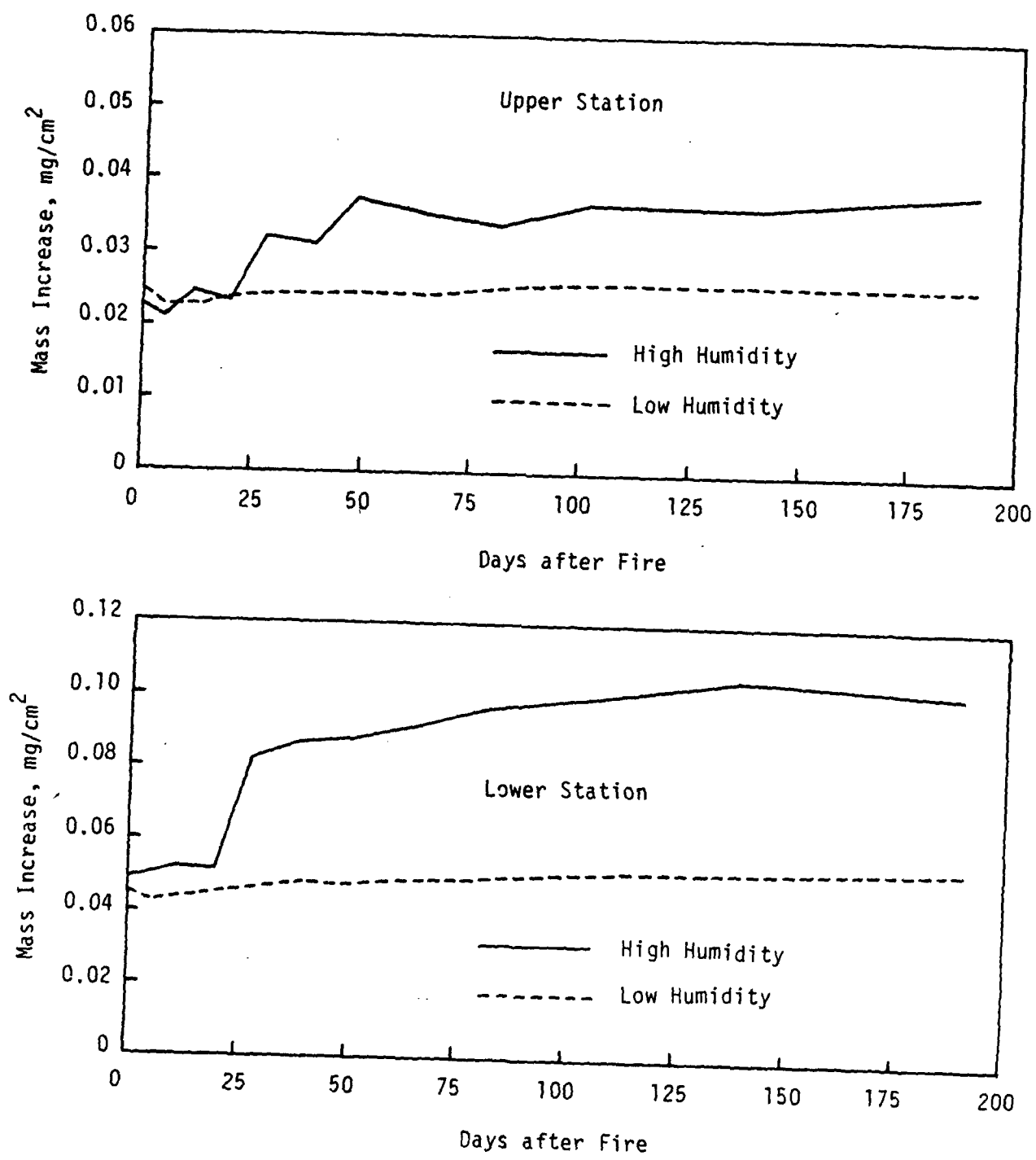
61

Figure 25. Mass Increases due to Corrosion for Monel 400 for Test W-13 (Nonflaming).
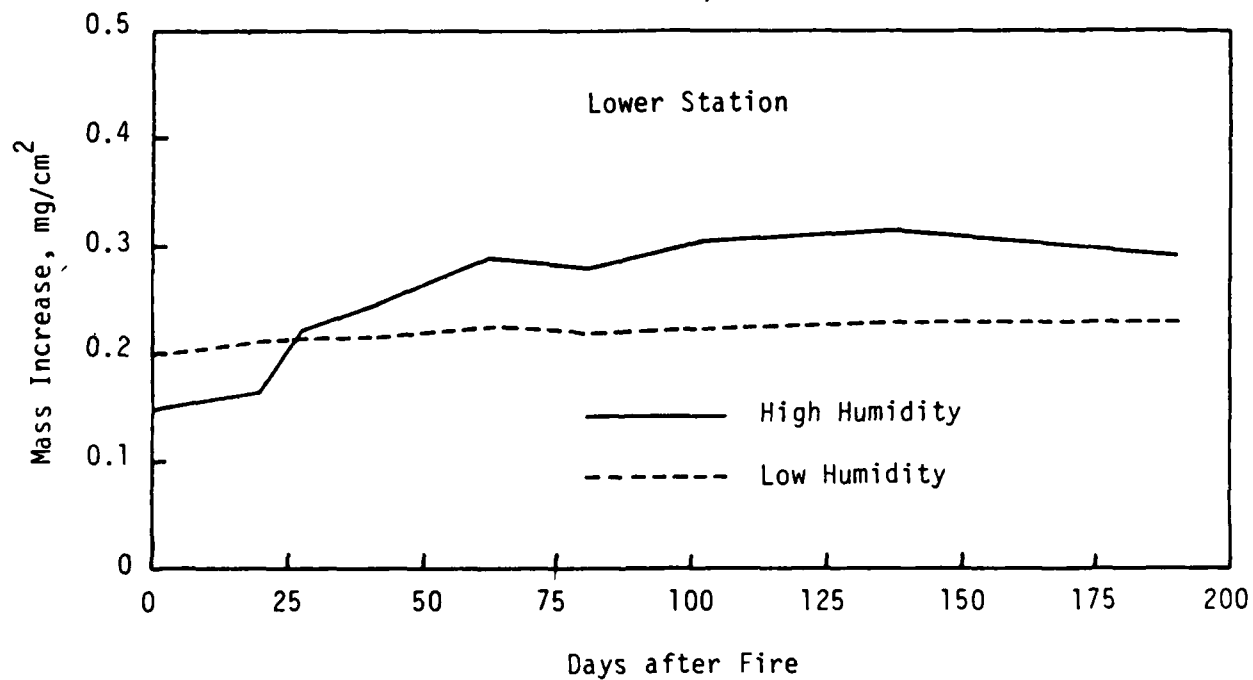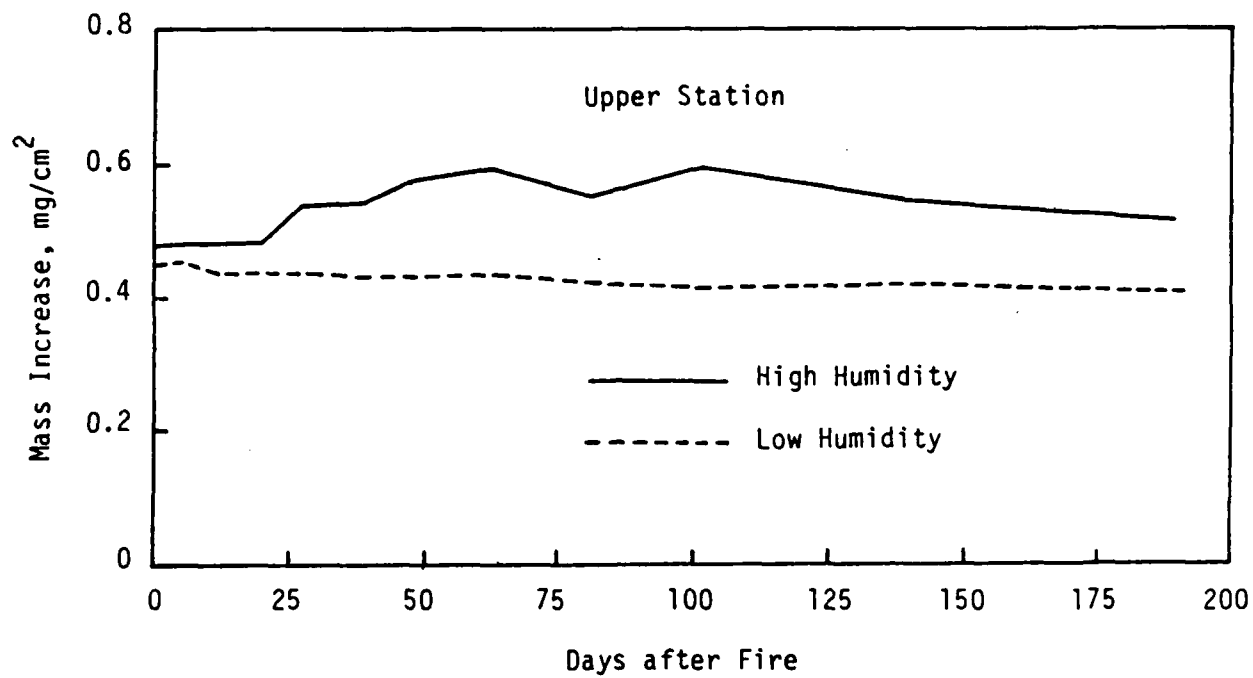
62

Figure 26. Mass Increases due to Corrosion for Monel 400 for Test W-13A (Flaming).

additional increase in mass of about 0.03 mg/cm^2 occurred during the first 8 days at 100% humidity followed by a more gradual increase in mass thereafter. For the corresponding specimens from the upper station, a more gradual mass increase of about 0.01 mg/cm^2 was observed. These mass increases incurred during the high humidity phase are again probably due to moisture adsorption by surface deposits. The gravimetric data for the W-13A (flaming) specimens are shown in Figure 26. For the low humidity specimens, little change in mass occurred during the post-fire period. The gradual mass decrease of 0.05 mg/cm^2 experienced by the specimens from the upper station can probably be attributed to losses of loosely adhering surface deposits during handling and weighing of these specimens. The gradual increase in mass of about 0.03 mg/cm^2 for the lower station specimens, however, is likely due to corrosion which is clearly visible on these specimens. For the specimens of the high humidity group, additional gradual mass increases of about 0.13 mg/cm^2 were observed during the initial half of the high humidity period. The control specimen, which was also exposed to high humidity, increased in mass by about 0.03 mg/cm^2 during the post-fire period.

The macroscopic corrosion features for the W-13A (flaming) Monel 400 specimens, along with the control specimen, are shown in Figure 27. The specimens from the upper station for both humidity groups were covered with an unbroken layer of fine soot particles with a sprinkling of large, fluffy, loosely adhering soot agglomerates. A few tiny greenish specks were also seen on some of the high humidity specimens. The specimens from the lower station were free of soot, but exhibited a dull grey surface with numerous round patches of tiny pale green crystals. These patches appear as small light spots in the photograph, and they range in size from roughly 100 microns to

Control

Upper
Station

Lower
Station

Low Humidity
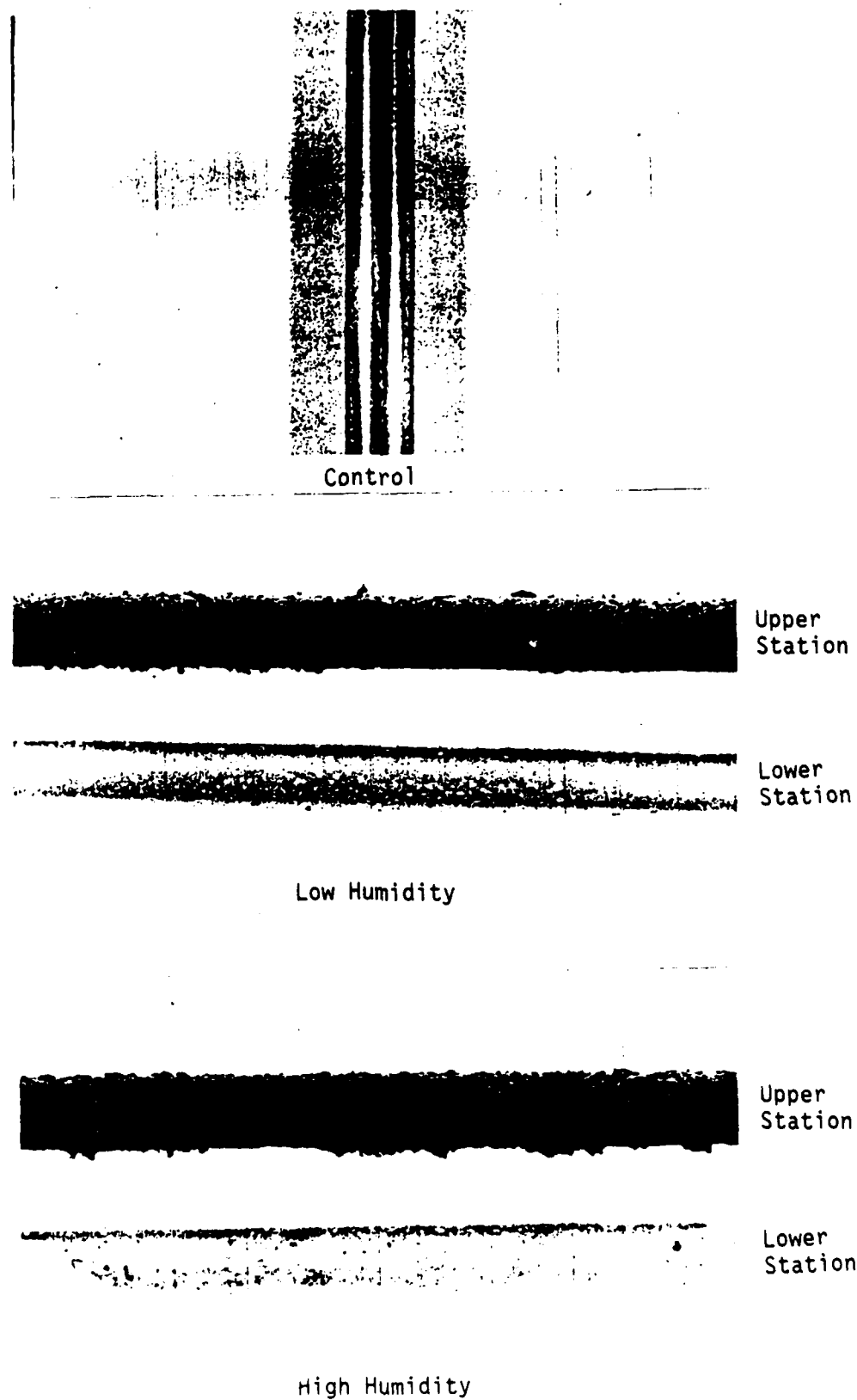
Upper
Station

Lower
Station

High Humidity

Figure 27. Macroscopic Corrosion Features for Monel 400
for Test W-13A (Flaming).

about 2000 microns. They are about equally numerous on specimens from both humidity groups. The pale green color indicates that these patches consist of nickel salts resulting from the reaction with acidic combustion products deposited on the surface. The characteristic blue-green color of copper salts was absent. The amount of corrosion products seen on the surface of the Monel 400 specimens was very small and did not cause any significant damage to this material.

The Monel 400 specimens from Test W-13 (nonflaming) appeared dull grey for both stations and for both humidity groups, except that the high humidity specimen from the lower station was sprinkled with tiny specks. The control specimen was a bright, shiny silver color with no evidence of corrosion.

At the end of the post-fire period the Monel 400 specimens were cleaned and weighed. For the W-13A specimens from the upper station, the layer of soot was gently scraped off with a razor blade, and the exposed surface was cleaned with methanol. This removed about 0.28 mg/cm^2 of material for the low humidity specimens and about 0.32 mg/cm^2 for the high humidity specimens. The cleaned surfaces of all of these specimens were heavily tarnished, ranging in color from bronze to dark brown. This tarnish was generally darker for the high humidity specimens. The high humidity specimens were also sprinkled with numerous tiny lighter colored spots, which were absent on the low humidity specimens. The tarnish resulted in a net mass increase of about 0.1 mg/cm^2 for the specimens in both humidity groups. For the W-13A specimens from the lower station, the pale green nickel salts were removed by rubbing with fine steel wool and wiping with tissue and methanol, but there was insufficient quantity of this material to collect a dry sample. The corrosion products

removed from the low humidity specimens was only about 0.31 mg/cm^2, while somewhat more, 0.39 mg/cm^2, was taken from the high humidity specimens. After cleaning, the surfaces of the lower station specimens of both humidity groups were dull grey with many tiny light patches where the nickel salts had been. The net mass decrease due to metal lost in the corrosion products during cleaning was roughly 0.10 mg/cm^2 for both humidity groups.

Summary

The gravimetric results of Test W-13 are summarized in Table 7. Of the four target materials exposed to the combustion products generated by nonflaming or smoldering combustion of the MIL-C-915E, Amend. 2 cables in Test W-13, only the HY80 steel experienced significant corrosion. For this material the corrosion products appeared to consist of hydrated ferric oxide, or rust, which was produced during both low and high humidity periods. The mass increases obtained during the first twenty days after the fire test at 70% humidity were about 25 times greater than the corresponding mass increases for the controls. During the period at 100% humidity (20-190 days), the mass increases due to corrosion were about five times greater than those for the specimens which remained at 70% humidity. The mass increases for the high humidity specimens were also about 8.5 times greater than the mass increase for the controls, which were also maintained at high humidity. The observed mass increases due to corrosion were not influenced significantly by the vertical location of the specimens in the fire compartment.

Of the remaining materials exposed in Test W-13, the brass and Monel 400 specimens exhibited small post-fire mass increases, especially in the 100%

Table 7. Incremental Weight Gains for Test W-13

Material	Station	Weight Increase During Period (mg/cm^2)		
		Low Humidity Period (0 - 20 days)	High Humidity Period (20 - 190 days)	
		Both Groups	L. H. Group	H. H. Group
HY80 Steel	1	0.592	0.391	2.160
	2	0.497	0.488	1.976
#304 Stainless Steel	1	0.0026	- 0.0013	0.0020
	2	0.0051	0.0013	0.0021
Brass	1	0.0028	0.0073	0.0154
	2	0.0003	0.0036	0.0135
Monel 400	1	- 0.0003	0.0024	0.0158
	2	0.0013	0.0084	0.0503

humidity environment. These mass increases appear to be due to the formation of thin oxide films or tarnish and the adsorption of water on their surfaces. The much smaller mass increases exhibited by the type 304 stainless steel specimens are consistent with the lack of visible evidence of corrosion for these specimens.

The gravimetric results of Test W-13A are summarized in Table 8. Of the four target materials tested, the HY80 steel specimens exhibited by far the greatest amount of corrosion due to exposure to the combustion products generated by flaming combustion of the MIL-C-915E Amend. 2 cables in Test W-13A. The corrosion products appeared to be a mixture of hydrated iron oxides. The vertical location of the coupons in the fire compartment had little effect on the post-fire mass increases in spite of dramatic differences in the quantity and composition of the surface deposits. During the first 20 days after the fire test (70% humidity), the mass increases for the Test W-13A specimens were about 60 times greater than those for the controls and about 2.5 times greater than those for the W-13 specimens. During the period at 100% humidity (20-190 days), the mass increases due to corrosion were about 12 times greater than the corresponding mass increases for the specimens which remained at 70% humidity. The mass increases for the high humidity W-13A coupons were also about 44 times greater than the mass increases for the controls and about five times greater than those for the corresponding W-13 coupons.

The brass specimens also experienced significant corrosion due to combustion products deposited during Test 13-A. This post-fire corrosion occurred only for the specimens from the upper location where heavy deposition of soot

Table 8.   Incremental Weight Gains for Test W-13A

Material	Station	Weight Increase During Period (mg/cm^2)		
		Low Humidity Period (0 - 20 days)	High Humidity Period (20 - 190 days)	
		Both Groups	L. H. Group	H. H. Group
HY80 Steel	1	1.428	0.793	9.996
	2	1.503	0.947	11.064
#304 Stainless Steel	1	- 0.0023	- 0.0143	- 0.0054
	2	0.0044	- 0.0041	- 0.0088
Brass	1	0.972	0.229	- 0.130
	2	- 0.0244	0.0147	0.1405
Monel 400	1	- 0.0055	- 0.0286	0.0326
	2	0.0145	0.0176	0.1266

and adsorption of water occurred during the fire test. For these specimens the corrosion products appeared to be a mixture of hydrated zinc and copper salts, probably chlorides, and a hard black coating of unknown composition. During the first 20 days of the post-fire period (70% humidity), the mass increase was about 500 times that of the controls, but this was largely due to moisture adsorption and hydration of salts. During the high humidity period (20-190 days) the mass changes were much smaller, and the mass loss for the high humidity group probably reflects losses of loosely adhering corrosion products during handling and weighing. For the low humidity brass specimens from the lower station the mass changes during the post-fire period were insignificant. For the high humidity specimens from the lower station the mass increase was about 32 times greater than the controls, due primarily to the formation of tarnish.

Of the remaining materials exposed to the combustion products generated during Test W-13A, only the high humidity Monel 400 specimens from the lower station exhibited appreciable mass increases due to corrosion. This mass gain amounted to about 3.4 times that of the control specimens which were also maintained at high humidity. This observation was consistent with the presence of numerous small patches of pale green nickel salts on these specimens. The other Monel 400 specimens and the #304 stainless steel specimens did not exhibit any significant mass changes during the post-fire period.

DISCUSSION AND CONCLUSIONS

A study was conducted to assess the post-fire corrosion hazard of the materials used in power and communications cables aboard ships to a number of metals used in shipboard structures and systems. Small metal specimens were exposed to the combustion products generated in full scale cable fire tests conducted at the U.S. Coast Guard Fire and Safety Test Detachment facility in Mobile, Alabama. Metal coupons were installed in the fire test compartment aboard an instrumented ship for three tests. In the first test (W-11), the fuel or source material was a mixture of two proposed new cables, MIL-C-24640 and MIL-C-24643. The other two tests involved a currently used cable, MIL-C-915E, Amendment 2. In the first of the MIL-C-915E tests (W-13), the cables failed to ignite and the metal specimens were exposed to the combustion products of smoldering or nonflaming combustion. In the second of the MIL-C-915E tests (W-13A), the cables ignited and the metals were exposed to the heavy sooty smoke produced during flaming combustion. The metallic specimens or target materials were HY80 steel, type 304 stainless steel, brass, and Monel 400. The metallic coupons were stored under both moderate and high humidity conditions after the fire tests. During this post-fire period, which lasted nearly a year, the specimens were weighed and observed periodically to assess the degree of corrosion.

Of the four target materials tested, the HY80 steel experienced the greatest amount of corrosion as assessed by mass increase, mass of corrosion products removed by cleaning, and macroscopic appearance. This was true for both the MIL-C-24640/24643 cables and the MIL-C-915E Amend 2 cables. The brass experienced significant corrosion only for the flaming MIL-C-915E Amend

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2 cables at the upper location. The Monel 400 specimens experienced only slight corrosion in the flaming MIL-C-915E Amend 2 test, while the type 304 stainless steel experienced little or no corrosion in all of the tests.

For the HY80 steel, the corrosion mass increases can be ranked in four groups in order of decreasing corrosion mass increase as follows:

(1) 10-11 mg/cm^2 MIL-C-915E Amend 2 cables, flaming, high humidity, upper and lower stations

(2) 2 mg/cm^2 MIL-C-915E Amend 2 cables, nonflaming, high humidity, upper and lower stations

(3) 0.4-1.0 mg/cm^2 MIL-C-915E Amend 2 cables, flaming, low humidity, upper and lower stations

MIL-C-915E Amend 2 cables, nonflaming, low humidity, upper and lower stations

MIL-C-24640/24643 cables, high humidity, upper and lower stations

(4) .005-.015 mg/cm^2 MIL-C-24640/24643 cables, low humidity, upper and lower stations

For the HY80 steel specimens, post-fire high humidity greatly accelerated the corrosion process for both the MIL-C-915E Amend 2 cables and the MIL-C-24640/24643 cables. A similar effect was noted for HY80 steel and cold rolled steel in a previous test conducted at the Naval Research Laboratory using PVC-nitrile rubber coated with intumescent paint as the source material (Ref. 1). These results are consistent with the observations of Vernon and

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others (Ref. 3) in studies of atmospheric corrosion whereby the corrosion process was greatly accelerated above a certain critical humidity, usually about 70%.

For the HY80 steel, vertical location of the test specimens in the fire test compartment had little effect on corrosion rates for all three tests. This is not surprising for the MIL-C-915E Amend 2 nonflaming test and the MIL-C-24640/24643 test, since the smoke levels were low and little stratification occurred. For the flaming MIL-C-915E Amend 2 test, the smoke density was much greater at the upper station which resulted in heavy deposition of soot on these specimens, but the corrosion rates were nearly the same as those for the specimens from the lower station.

For the HY80 steel specimens, the corrosion products consisted of various hydrated ferric oxides, namely, rust. Thus it appears that the presence of chloride ions, which result from the combination of HCl and moisture, accelerate the rusting process in a manner similar to the electrolytic action of chloride ions when ferrous metals are exposed to sea spray. A discussion of this mechanism is given in Ref. 4.

For the brass specimens, significant corrosion occurred only for the flaming MIL-C-915E Amend 2 test at the upper location. Most of the mass increase occurred during the fire test and immediately thereafter, although corrosion products were not seen at that time. The wet black coating seen immediately after the fire probably contained large quantities of water attracted by hygroscopic corrosion products formed below the soot layer. This water probably accounted for the large initial mass increase of these specimens. Later as the blue-green and white crystalline material appeared, this water was incorporated into the corrosion products as water of

crystallization. Likely candidates for the corrosion products are copper chloride dihydrate, $CuCl_2 \cdot 2H_2O$, which is blue-green, and zinc chloride, $ZnCl_2$, which is white and deliquescent (Ref. 5). During the post-fire period, little additional mass increase occurred, which indicates that the corrosion products became saturated early and little additional moisture was adsorbed during the post-fire period. This would also account for the small effect of humidity on these specimens.

For the brass specimens from the lower rack which were exposed to the combustion products generated during the flaming MIL-C-915E Amend 2 cable test, the mass increases were only 10% as great as those experienced by the upper rack specimens. No crystalline corrosion products were visible on the specimens; instead, they were coated with a dark tarnish.

Brass specimens from the nonflaming MIL-C-915E Amend 2 test and the MIL-C-24640/24643 test exhibited various degrees of discoloration due to tarnish and interference tints, which indicate the formation of thin oxide or sulfide films. Such films are usually formed at high temperatures and are known to inhibit further corrosion. For these tests the mass increases of the specimens were small and damage to the material was insignificant.

The Monel 400 was fairly resistant to corrosion from exposure to the combustion products of both source materials. Visible corrosion was experienced only for the flaming test of the MIL-C-915E Amend 2 cables. At the lower station minute quantities of pale green crystalline material was visible, which was probably nickel chloride hexahydrate, $NiCl_2 \cdot 6H_2O$ (Ref. 5). The

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specimens from the upper station were coated with a dark brown tarnish, which was visible after removal of the sooty deposits.

The type 304 stainless steel was the most resistant to corrosion induced by the combustion products of the source materials. Only for the flaming test of the MIL-C-915E Amend 2 cables was a trace of corrosion products visible. At the upper station thin film oxidation occurred as evidenced by slight tarnish and interference tints. At the lower station microscopic quantities of rust were observed.

The results of this study show that the older type cables present a severe corrosion hazard to some commonly used metals when exposed to their corrosion products in a fire. The corrosion problem is most serious when the metals are in a high humidity environment after the fire. This study also showed that by using new cable materials which produce less smoke and corrosive gas, the corrosion hazard can be greatly reduced.

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